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VOLUME IV

Alternate Concepts for SO_x, NO_x, and Particulate Emissions Control From a Fuel-Rich Precombustor

J. F. LaFond, J. A. Cole, W. C. Li, E. C. Moller, R. Payne
(Energy and Environmental Research Corporation)

and

P. W. Waanders
Babcock & Wilcox
20 S. Van Buren Avenue
Barberton, OH 44203

EPA Contract 68-02-3130

EPA Project Officer: P. Jeff Chappell
Air and Energy Engineering Research Laboratory
Research Triangle Park, NC 27711

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16. ABSTRACT

The report gives results of a study of the use of precombustors for the simultaneous control of SO_2, NOx, and ash emissions from coal combustion. In Phase 1, exploratory testing was conducted on a small pilot scale--293 kW (million Btu/hr)--pulverized-coal-fired precombustor to identify critical operating parameters. The results from this testing raised several questions regarding the viability of controlling SO_2 emissions by injecting calcium-based sorbent materials, under conditions simultaneously conducive to NOx control, and to the rejection of coal ash as a molten slag. In Phase 2, key elements of the sulfur capture process, under the fuel-rich precombustor conditions necessary to control NOx formation, were investigated. Detailed experimental studies were conducted at bench and laboratory scales to: (1) investigate the formation of stable sulfides in the entrained flow region of a precombustor, using calcium-based sorbents; (2) study the evolution of sulfur from coal under entrained flow combustion conditions; and (3) investigate the stability of sulfur species in molten slag layers. Study results indicated that the sulfidation reactions between CaO and H_2S or COS are fast and, under optimum conditions, can remove a high fraction of the gas-phase sulfur species in a fuel-rich precombustor.

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a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Calcium	Pollution Control	13B
Coal	Electric Utilities	Stationary Sources	21D
Combustion		Particulate	21B
Sulfur Dioxide		Precombustors	07B
Nitrogen Oxides			
Particles			14G

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ABSTRACT

This report describes the results of a study related to the use of precombustor concepts for the simultaneous control of SO_2, NO_x and ash emissions from coal combustion. In a first phase of the study, exploratory testing was conducted on a small pilot scale (293 kW--1 x 10^6 Btu/hr) pulverized-coal-fired precombustor to identify critical operating parameters. The results from this testing raised several questions regarding the viability of controlling SO_2 emissions through the injection of calcium-based sorbent materials, under conditions simultaneously conducive to NO_x control, and to the rejection of coal ash as a molten slag.

In a second phase of the study key elements of the sulfur capture process, under the fuel-rich precombustor conditions necessary to control NO_x formation, were investigated. Detailed experimental studies were conducted at bench and laboratory scales in order to: 1) investigate the formation of stable sulfides in the entrained flow region of a precombustor using calcium based sorbents, 2) study the evolution of sulfur from coal under entrained flow combustion conditions, and 3) investigate the stability of sulfur species in molten slag layers.

Results from the study indicated that the sulfidation reactions between CaO and H_2S or COS are fast, and under optimum conditions can remove a high fraction of the gas phase sulfur species in a fuel-rich precombustor. However, typical coal ash and ash/CaO mixtures were found to have a low capacity for retaining large amounts of sulfur under equilibrium conditions in a precombustor environment. In order to achieve significant fuel-rich sulfur capture, the implication for practical precombustor systems is that rapid slag drainage systems are required, or that slag fluxing additives may be necessary.

The work described in this report has been supported by the United States Environmental Protection Agency through Contract No. 68-02-3130 to Babcock and Wilcox (B&W) and to Energy and Environmental Research Corporation under B&W subcontract No. 940962NR.

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TABLE OF CONTENTS

Section Page

1.0 PROGRAM SUMMARY. 1-1
1.1 Introduction. 1-1
1.2 Scope 1-3
1.3 Experimental Systems. 1-4
1.4 Results 1-4
1.5 Conclusions 1-21

2.0 INTRODUCTION 2-1
2.1 Precombustor Concept. 2-1
2.2 Sulfur Control. 2-3
2.3 Program History 2-8

3.0 BACKGROUND 3-1
3.1 Precombustor Experience 3-1
3.2 Review of Slag Related Industry and Research. 3-15
3.3 Calcium Sulfidation 3-30

4.0 OBJECTIVES AND APPROACH. 4-1

5.0 EXPERIMENTAL SYSTEMS 5-1
5.1 Isothermal Reactor (ITR). 5-1
5.2 Control Temperature Tower (CTT) 5-5
5.3 High Temperature Oven (HTO) 5-9
5.4 Continuous Flue Gas Sampling System 5-13
5.5 Reduced Sulfur Species Sampling System. 5-17
5.6 Solid Sampling Techniques 5-17
5.7 Sorbent Feeding 5-21
5.8 Temperature Measurement 5-21
5.9 Test Material Compositions. 5-21

TABLE OF CONTENTS (Continued)

Section Page

6.0 ENTRAINED FLOW SULFIDATION RESULTS 6-1
  6.1 Isothermal -- Gas-Fired 6-1
    6.1.1 Fuel Effects 6-1
    6.1.2 Impact of H_2S Injection Location 6-3
    6.1.3 Time-Resolved Capture. 6-7
    6.1.4 Stoichiometry Effects. 6-7
    6.1.5 Temperature Effects. 6-9
    6.1.6 Impact of Sorbent Type 6-9
    6.1.7 Gas Phase Versus Solids Sampling 6-14
    6.1.8 Comparison of Fuel-Rich to Fuel-Lean Capture. 6-14
  6.2 Slow Quench Rate -- Coal-Fired. 6-14
    6.2.1 Stoichiometry Effects. 6-16
    6.2.2 Load Effects 6-22
    6.2.3 Impact of Sorbent Type and Feed Rate 6-22
    6.2.4 Effect of Injection Temperature. 6-27

7.0 SLAG SULFUR CHEMISTRY RESULTS. 7-1
  7.1 Sulfur Solubility and Equilibrium 7-1
  7.2 Impact of Slag Fluxing Additives. 7-10
  7.3 Slag Desulfurization Rates. 7-14
  7.4 In-Situ Sulfur Capture in Slag. 7-17

8.0 QUALITY CONTROL EVALUATION 8-1
  8.1 Instrument Accuracy and Precision 8-1
  8.2 System Uncertainties and Data Completeness. 8-1

9.0 CONCLUSIONS. 9-1

10.0 RECOMMENDATIONS. 10-1

TABLE OF CONTENTS (Concluded)

Section Page

11.0 ACKNOWLEDGEMENTS. 11-1

12.0 REFERENCES. 12-1

APPENDIX A -- QUALITY ASSURANCE/QUALITY CONTROL (QA/QC) A-1

- A.1 EXPERIMENTAL SYSTEMS. A-1
  - A.1.1 Gas Species Sampling. A-1
  - A.1.2 Solids Sampling A-6
  - A.1.3 Temperature Measurements. A-6
  - A.1.4 Gas Flow Metering A-16
  - A.1.5 Sorbent Feed Rate A-16
- A.2 ANALYTICAL. A-17
  - A.2.1 Continuous Gas Species Analysis . A-17
  - A.2.2 Gas Chromatography Analysis . . . A-17
  - A.2.3 Solids Analysis A-17
  - A.2.4 Data Representativeness and Completeness. A-22
- A.3 CALIBRATION PROCEDURES. A-23
- A.4 DATA REDUCTION. A-33
  - A.4.1 Calcium Utilization A-33
  - A.4.2 Sulfur Capacity A-35
  - A.4.3 Equilibrium Sulfur Capture by Slag. A-36
  - A.4.4 Furnace Residence Time. A-36

APPENDIX B -- EXAMPLES OF RAW DATA. B-1

- B.1 ITR Data Example B-2
- B.2 CTT Data Example. B-7
- B.3 HTO Data Example. B-24

LIST OF FIGURES

Figure | Page

1-1 Common cyclonic precombustor in staged combustion configuration attached to boiler furnace wall 1-2

1-2 Sulfur speciation in the ITR at 1100°C, SR=0.83 when either mixing 5000 ppm H_2S with the fuel (C_2H_4) or injecting it downstream of the flame. 1-5

1-3 Calcium utilization in the ITR using Linwood atmospheric hydrate, measured by both gas and solid analysis. 1-6

1-4 Calcium utilization in the ITR at SR=0.83 when injecting 5000 ppm H_2S downstream of a C_2H_4 flame 1-7

1-5 Calcium utilization in the ITR under fuel-rich and fuel-lean conditions for both Linwood atmospheric hydrate and Vicron 45-3 limestone 1-9

1-6 Sulfur speciation in the CTT firing Illinois coal at 17.6 kW (60,000 Btu/hr). 1-10

1-7 Calcium utilization in the CTT firing Illinois coal at 17.6 kW (60,000 Btu/hr), injecting Linwood atmospheric hydrate at about Ca/S = 1.0 1-11

1-8 Species evolution from Illinois coal in the CTT at 17.6 kW (60,000 Btu/hr). 1-12

1-9 Capture of total sulfur in the CTT by the injection of sorbents when firing Illinois coal at 23.4 kW (80,000 Btu/hr), SR=0.6 1-13

1-10 Influence of temperature and molar basicity on sulfur capacity for several slag mixtures 1-14

1-11 Equilibrium sulfur removal by slag for SR=0.5, T=1200°C, and an Illinois coal with 3.97% sulfur. 1-16

1-12 Equilibrium sulfur removal by slag for SR=0.5, T=1400°C, and an Illinois coal with 3.97% sulfur. 1-17

1-13 Fluid and T_{250} temperatures for Illinois coal ash/CaO mixtures. 1-18

1-14 Influence of fluxing additives on the reducing fluid temperature of Illinois coal ash and CaO mixtures 1-19

1-15 Desulfurization of CaS and Illinois coal ash slag mixtures, showing the influence of calcium content and mixedness 1-20

LIST OF FIGURES (Continued)

Figure Page

2-1 Common cyclonic precombustor in staged combustion configuration attached to boiler furnace wall 2-2

2-2 Equilibrium stability of solid calcium-sulfur compounds . . 2-4

2-3 Calcium sulfate formation at elevated injection temperatures. 2-5

2-4 Schematic diagram of some of the important mechanisms occurring in a fuel-rich precombustor system with sorbent addition. 2-7

3-1 Precombustor arrangement and refractory detail. 3-3

3-2 Mean gas temperatures and bulk residence times in the precombustor and furnace (SR_1 = 0.5, 0.3 MW_t) 3-4

3-3 Equilibrium distribution of sulfur species under the reducing conditions of the precombustor for Illinois coal with and without calcium present 3-5

3-4 Stack NO_x emissions as a function of SR_1 for Illinois coal and natural gas (SR_T = 1.2) 3-6

3-5 Sulfur capture when firing natural gas (0.3 MW_t) and injecting Vicron 45-3 and dolomite with the primary air at Ca/S = 2 (SR_T = 1.2) 3-8

3-6 SO_2 capture based on gas phase stack measurements and potential SO_2 capture based on calcium utilization of solids samples 3-9

3-7 Effect of increased solids removal on sulfur capture for two fuels. Vicron 45-3 injected with primary air (SR_1 = 0.5, 0.3 MW_t) 3-10

3-8 Effect of sorbent additive (5% Fe_2O_3 by weight) on sulfur capture, sorbent injected with primary air (natural gas, SR_1 = 0.5, 0.3 MW_t) 3-12

3-9 Cross-section of the VCC prototype combustor (0.9 MW_t). . . 3-13

3-10 Recent ash retention efficiency measurements and system pressure drop versus firing rate (La Fond et al., 1986) in the VCC 3-14

3-11 NO_x control by combustion staging and natural gas reburning in the VCC; Illinois coal, SR_T = 1.2. 3-16

LIST OF FIGURES (Continued)

Figure Page

3-12 Effect of stoichiometry and Ca/S molar ratio on sulfur capture when injecting sorbent into the VCC under staging conditions. 3-17

3-13 Cross-sectional view of blast furnace 3-18

3-14 Iron desulfurization process schematic. 3-20

3-15 Ladle positions in the production of steel by the basic oxygen furnace. 3-21

3-16 Sulfur capacities, at 1650°C, in $CaO-SiO_2-Al_2O_3$ melts . . . 3-23

3-17 Desired slag compositions in the Armco top slag desulfurization process 3-24

3-18 Ternary diagram for $CaO-Al_2O_3-SiO_2$ melts; temperature in °C 3-25

3-19 Ternary diagram for $FeO-Al_2O_3-SiO_2$ melts; scales in weight percent and temperature in °C 3-26

3-20 Ternary diagram for $FeO-Na_2O-SiO_2$ melts; scales in weight percent and temperature in °C 3-29

3-21 Sulfur capacities C_s, in various slag systems at 1650°C . . 3-31

3-22 Comparison of sulfur capture capability for four different sorbent materials under fuel-lean conditions. . . 3-33

4-1 Program approacn flow-chart 4-2

5-1 Schematic of the isothermal reactor (ITR) 5-2

5-2 Schematic detail of the precombustor/sliding burner assembly 5-3

5-3 Cross-sectional views of the CTT configured with a fuel-rich zone 5-6

5-4 Multi-layer refractory design of the CTT. 5-7

5-5 Premixed burner 5-8

LIST OF FIGURES (Continued)

Figure		Page
5-6	Temperature profiles measured in the fuel-rich zone of the CTT for three different operating conditions when burning Illinois coal	5-10
5-7	High temperature oven test facility with gas blending capability	5-11
5-8	High temperature oven facility temperature distributions	5-14
5-9	Phase discrimination probe tip	5-15
5-10	Continuous monitoring flue gas sampling system	5-16
5-11	SO_2 continuous monitoring and batch sampling system	5-18
5-12	Isokinetic solids sampling probe with upper and lower cooling jackets used in the ITR	5-19
5-13	Solid sampling system used on the CTT	5-20
5-14	Fine-wire thermocouple probe for gas temperature measurements in the ITR	5-22
5-15	Gas temperature measurement system for the CTT	5-23
5-16	Comparison of sorbent size distributions as measured by x-ray sedigraph technique	5-25
6-1	Sulfur speciation in the ITR at 1100°C, SR = 0.83 when doping CH_4 and C_2H_4 with approximately 5000 ppm H_2S	6-2
6-2	Calcium utilization in the ITR using Linwood atmospheric hydrate, measured by both gas and solids analysis	6-4
6-3	Sulfur speciation in the ITR at 1100°C, SR = 0.83 when either mixing 5000 ppm H_2S with the fuel (C_2H_4) or injecting it downstream of the flame	6-5
6-4	Calcium utilization in the ITR using Linwood atmospheric hydrate, measured by both gas and solid analysis	6-6
6-5	Sulfur speciation with and without sorbent present in the ITR at 1100°C, SR - 0.83	6-8
6-6	Sulfur speciation in the ITR at 1100°C when injecting 5000 ppm H_2S downstream of the C_2H_4 flame	6-10

LIST OF FIGURES (Continued)

Figure		Page
6-7	Sulfur speciation in the ITR at sr = 0.83 when injecting 5000 ppm H_2S downstream of the C_2H_4 flame	6-11
6-8	Calcium utilization in the ITR at SR = 0.83 when injecting 5000 ppm H_2S downstream of a C_2H_4 flame	6-12
6-9	Calcium utilization in the ITR at 1100°C, SR = 0.83 with 5000 ppm H_2S injected downstream of the C_2H_4 flame.	6-13
6-10	Calcium utilization in the ITR under fuel-rich and fuel-lean conditions for both Linwood atmospheric hydrate and Vicron 45-3 limestone	6-15
6-11	Sulfur speciation in the CTT firing Illinois coal at 17.6 kW (60,000 Btu/hr)	6-17
6-12	Calcium utilization in the CTT firing Illinois coal at 17.6 kW (60,000 Btu/hr), injecting Linwood atmospheric hydrate at about Ca/S = 1.0	6-18
6-13	Species evolution from Illinois coal in the CTT at 17.6 kW (60,000 Btu/hr).	6-19
6-14	Comparison of measured gas phase sulfur speciation from an SR = 0.8 Illinois coal flame to equilibrium speciations calculated at conditions which correspond to the local measured stoichiometry and temperature	6-21
6-15	Calcium utilization in the CTT firing Illinois coal at SR = 0.6 injecting Linwood atmospheric hydrate at about Ca/S = 1.0	6-23
6-16	Species evolution from Illinois coal in the CTT at SR = 0.6	6-24
6-17	Sulfur speciation in the CTT firing Illinois coal at SR = 0.6.	6-25
6-18	Capture of total sulfur in the CTT by the injection of sorbents when firing Illinois coal at 23.4 kW (80,000 Btu/hr), SR = 0.6	6-26
6-19	Capture of gas phase sulfur in the CTT by the injection of sorbents when firing Illinois coal at 23.4 kW (80,000 Btu/hr), SR = 0.6.	6-28

LIST OF FIGURES (Continued)

Figure		Page
6-20	Calcium utilization as a function of Linwood atmospheric hydrate injection temperature in the CTT firing Illinois coal at 23.4 kW (80,000 Btu/hr), SR = 0.6	6-29
7-1	Slag exposure time requirements for Illinois coal ash/CaO slag corresponding to a Ca/S = 2 at 1400_0C, SR = 0.5. .	7-3
7-2	Influence of temperature and molar basicity on sulfur capacity for several slag mixtures	7-5
7-3	Sulfur capacity for iron silicate melts at various initial slag molar basicities	7-6
7-4	Equilibrium sulfur removal by slag for SR=0.5, T=1200°C, and an Illinois coal with 3.97% sulfur.	7-7
7-5	Equilibrium sulfur removal by slag for SR = 0.5, T = 1400°C, and an Illinois coal with 3.97% sulfur.	7-9
7-6	Fluid and T_{250} temperatures for Illinois coal ash/CaO mixtures.	7-11
7-7	Influence of fluxing additives on the reducing fluid temperature of Illinois coal ash and CaO mixtures	7-12
7-8	Desulfurization of CaS and Illinois coal ash slag mixtures, showing the influence of calcium content and mixedness	7-15
7-9	Desulfurization of CaS/Illinois coal ash/additive slag mixtures	7-16
7-10	Desulfurization plot of CaS and Illinois coal ash mixtures plotted to obtain the rate constants presented in Table 7-3.	7-18
A-1	SO_2 continuous monitoring and batch sampling system	A-2
A-2	Continuous monitoring flue gas sampling system.	A-4
A-3	SO_2 continuous monitoring and batch sampling system	A-5
A-4	Depletion of sulfur species within a tedlar sample bag as a function of storage time	A-7
A-5	Isokinetic solids sampling probe with upper and lower cooling jeckets used in the ITR	A-8

LIST OF FIGURES (Concluded)

Figure Page

A-6 Solid sampling system used on the CTT A-9

A-7 Fine-wire thermocouple probe for gas temperature measurements in the ITR A-10

A-8 Gas temperature measurement system for the CTT. A-14

A-9 Suction pyrometer aspirator pressure calibration for CTT. . A-15

A-10 Example of daily standard checks for the gas chromatograph during one calibration period A-20

A-11 H_2S calibration curves for 70, 50 and 30 l syringe injection A-26

A-12 SO_2 calibration curves for 70, 50 and 30 l syringe injection A-27

A-13 COS calibration curve for 70 l syringe injection A-28

A-14 CS_2 calibration curve for 70 l syringe injection A-29

A-15 Gas chromatograph printout example. A-30

A-16 Gas chromatograph printout example. A-31

A-17 Gas chromatograph printout example. A-32

LIST OF TABLES

Table		Page
3-1	Effect of B_2O_3 Substitutions on Melting Time for the Na_2O-CaO-B_2O_3-SiO_2 System	3-28
5-1	Temperature Variation in the ITR at a Nominal 900°C Isothermal Condition	5-4
5-2	Feed Gas Compositions	5-12
5-3	Properties of Vicron Limestone and Linwood Atmospheric Hydrate	5-24
5-4	Illinois Coal Composition and Heating Value	5-27
5-5	Mineral Analysis of Illinois Coal Ash	5-28
5-6	Compositions of CaO/Ash and Fe_2O_3/Ash Mixtures	5-29
7-1	Feed Gas Compositions	7-2
7-2	Influence of Slag Additives on Sulfur Capacity Ca/S = 1; log C_s Determined at 1400°C, SR = 0.5	7-13
7-3	Desulfurization Rate Constants for CaS/Illinois Coal Ash Mixtures	7-19
8-1	Precision and Accuracy for Analysis Instruments and Techniques	8-2
A-1	Radial Temperature Change in the ITR at a Nominal 900°C Isothermal Condition	A-13
A-2	CTT Instrumentation	A-18
A-3	Precision, Accuracy and Completeness Data for Continuous Monitoring Gas Species Instruments	A-19
A-4	Solid Analyses Precision and Accuracy Data	A-21
A-5	Calibration Procedures	A-24
A-6	Calibration Gases	A-25

1.0 PROGRAM SUMMARY

1.1 Introduction

The potential for simultaneous control of ash, NO_x and SO_x emissions from coal-fired boilers and heaters by combustion exterior to the furnace entry has made precombustor development an area of great interest and effort. A precombustor burns coal in a chamber outside the normal furnace region. An example of a simple precombustor scheme is presented in Figure 1-1.

Aerodynamic separation and slag drainage removes a majority of the coal mineral matter before entry into the furnace. Also, staged combustion and reburning have been shown to be effective means of controlling NO_x emissions. It has been proposed that the use of calcitic sorbent or possibly other additives in a fuel-rich precombustor can produce significant reductions in overall SO_2 emissions. Successful control of all three pollutants would allow coal users to circumvent expensive exhaust stream clean-up equipment and help avoid derating in oil or gas retrofit applications.

The issue of sulfur capture under fuel-rich conditions has been an area of uncertainty and much recent interest. The fuel-rich reactions of:

$$H_2S + CaO \longrightarrow CaS + H_2O \text{ or}$$
$$COS + CaO \longrightarrow CaS + CO_2 \text{ ,}$$

are theoretically more effective at capturing gas phase sulfur than the well studied fuel-lean reaction:

$$SO_2 + CaO + 1/2\ O_2 \longrightarrow CaSO_4 \text{ ,}$$

both from a thermodynamic and kinetic standpoint. However, at the time this program was initiated the operating conditions which promote these fuel-rich reactions had not been fully investigated. In addition, the presence of a liquid slag in the reactor was thought to be a potential source of sulfur capture or regeneration which required additional research.

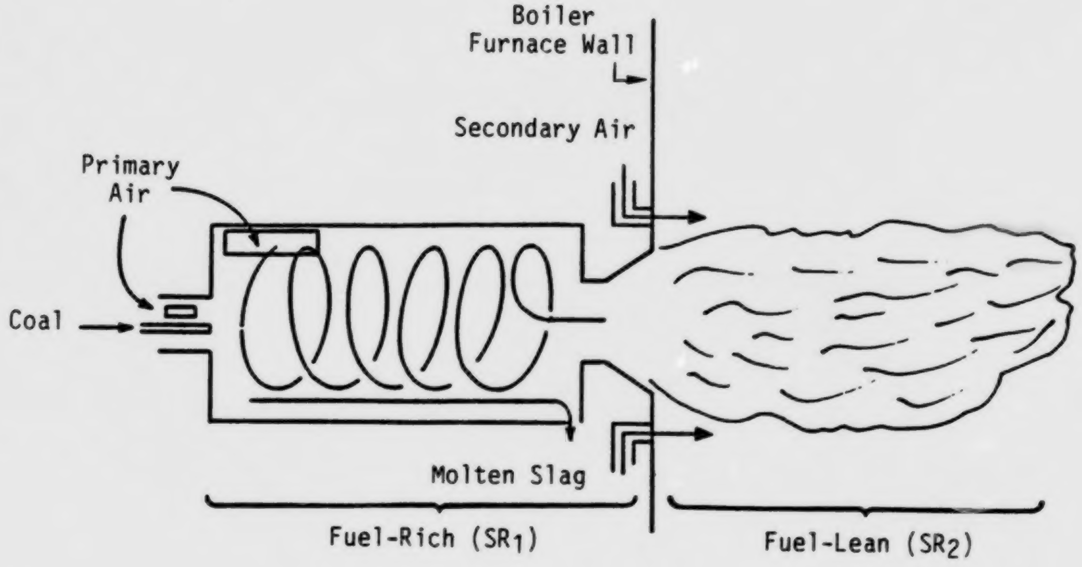

Boiler
Furnace Wall
Secondary Air
Primary
Air
Coal
Molten Slag
Fuel-Rich (SR_1)
Fuel-Lean (SR_2)

Figure 1-1. Common cyclonic precombustor in staged combustion configuration attached to boiler furnace wall.

Efforts in this program have focused on both entrained flow sorbent sulfidation by dry powder injection and the interaction of sulfur, coal ash and additives in molten slags under fuel-rich conditions.

The work described in this report has been supported by the United States Environmental Protection Agency through Contract No. 68-02-3130 to Babcock and Wilcox (B&W) and to Energy and Environmental Research (EER) under B&W subcontract No. 940962NR.

1.2 Scope

The program involved two phases. The first phase consisted of exploratory testing of a pilot scale coal precombustor (293 kW (1 x 10^6 Btu/hr)) to help identify critical operating parameters for precombustor systems with NO_x control and the potential for sulfur control.

The pilot-scale testing indicated that there was significant sulfur captured as calcium sulfide (CaS) by suspended sorbent particles in the fuel-rich combustion zone of the precombustor. However, there was evidence that sulfur was released from the CaS when exposed to a fuel-lean flame front. There was also concern that sulfur in the slag layer was evolving back into the gas phase. A combination of high solids carryover, complexities of sampling in the pilot-scale precombustor, and a growing number of fundamental questions concerning fuel-rich sulfur capture led to the second phase of this program which is the main topic of this final report.

The objective of this second phase of work was to make a detailed investigation of several key elements in the fuel-rich sulfur capture process, including: 1) the formation of stable sulfides in the entrained flow region of a precombustor using calcium-based sorbents, 2) the evolution of sulfur from coal in an entrained flow process, and 3) the stability of sulfur in molten slag layers.

1.3 Experimental Systems

Three facilities were utilized in the program: 1) the Isothermal Reactor (ITR) to investigate particular sulfidation reactions and to identify key operating conditions in a well-controlled gas-flame environment, 2) the Control Temperature Tower (CTT) for investigation of sulfur evolution from coal and sulfidation in a coal combustion environment, and 3) the High Temperature Oven (HTO), a new facility, for the study of sulfur and slag interaction.

Two calcitic sorbents were tested in the entrained flow studies, Linwood atmospheric hydrate ($Ca(OH)_2$) and Vicron carbonate ($CaCO_3$). Methane and ethylene doped with H_2S were used in the ITR studies while natural gas and Illinois coal were used on the CTT. The slag studies used mixtures of Illinois coal ash and pure CaO and CaS.

1.4 Results

On the ITR facility the impact of fuel type, H_2S doping location (to change the reactor sulfur speciation), stoichiometry, temperature and sorbent type were investigated at isothermal conditions. Sulfur capture was determined using both gas phase and solids measurements. The gas phase sulfur speciation was determined by gas chromatography over a variation in residence time of about 0.25 to 1.0 seconds.

Figures 1-2 and 1-3 show how drastically the sulfur speciation is effected by moving the dopant H_2S downstream of the reactor flame and the corresponding increase in calcium utilization when more H_2S is available for reaction.

When operating at temperatures more favorable for slag formation, in the range of $1300^{o}C$ ($2372^{o}F$), calcium utilization dropped significantly compared to capture results at $1100^{o}C$ ($2012^{o}F$), as shown in Figure 1-4.

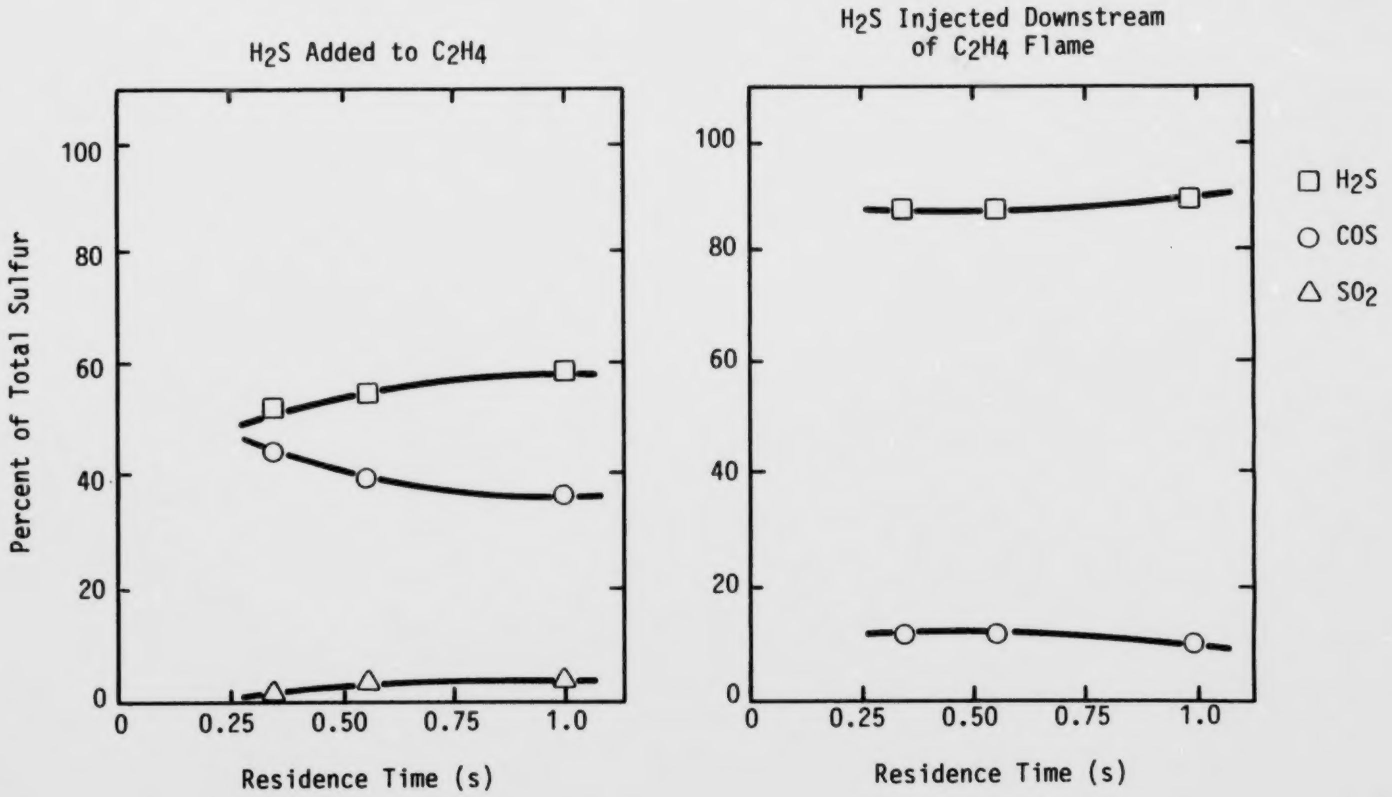


Figure 1-2. Sulfur speciation in the ITR at 1100°C, SR = 0.83 when either mixing 5000 ppm H_2S with the fuel (C_2H_4) or injecting it downstream of the flame.

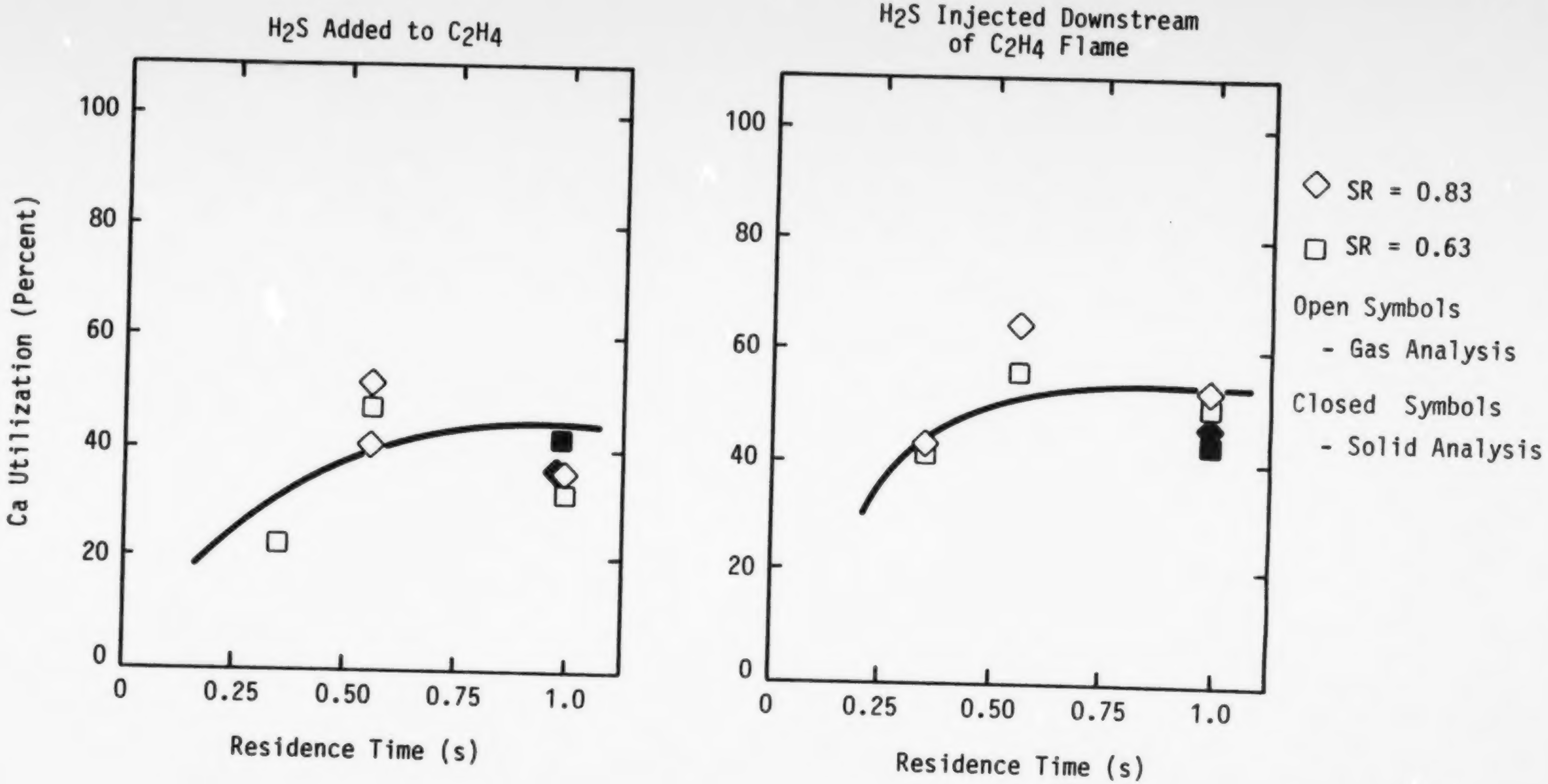


Figure 1-3. Calcium utilization in the ITR using Linwood atmospheric hydrate, measured by both gas and solid analysis. ITR held at 1100°C when doping the fuel (C_2H_4) with 5000 ppm H_2S or injecting it downstream of the flame ($Ca/S \simeq 1.0$ for each case).

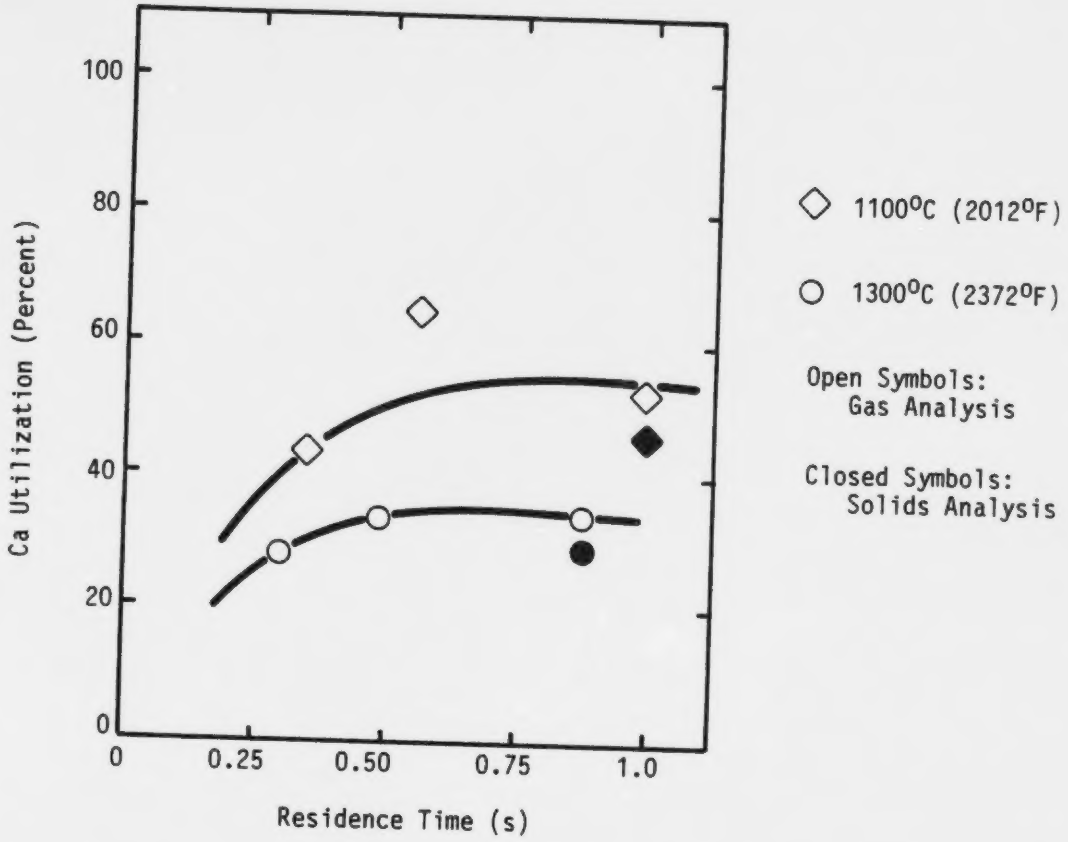


Figure 1-4. Calcium utilization in the ITR at SR = 0.83 when injecting 5000 ppm H_2S downstream of a C_2H_4 flame. Sorbent was Linwood atmospheric hydrate with Ca/S $\simeq$ 1.0 for each case.

In general, these utilization results are much greater than fuel-lean results at similar temperature and injection conditions using the same sorbents (see Figure 1-5). Also, Figure 1-5 shows that the relative reactivity of Linwood hydrate and Vicron carbonate is similar under fuel-rich conditions as compared to fuel-lean conditions. This suggests that information gained is studying sorbent properties and reactivity under fuel-lean conditions can be applied to the fuel-rich capture problem.

Sorbent injection while firing Illinois coal on the CTT at stoichiometric ratios of 0.6 and 0.8 produced drastically different sulfur speciation and utilization levels as seen in Figures 1-6 and 1-7. Figure 1-7 shows how successful entrained flow sulfidation can be for controlling sulfur under coal-firing conditions at controlled stoichiometry and temperature. However, solid sampling revealed that these same conditions were not favorable for entrained flow carbon burnout (see Figure 1-8).

Test results on the CTT again showed that Linwood was much more effective than Vicron under fuel-rich conditions. Figure 1-9 shows that at least 60 percent of the total input sulfur can be removed by the injection of Linwood atmospheric hydrate at a Ca/S molar ratio of 1.5-2.0. This 60 percent value does not take into consideration the sulfur that remains in char form. Capture would undoubtedly be higher if all the fuel-bound sulfur evolved immediately into the gas phase.

Sulfur solubility in coal ash slags was tested for a variety of CaO/ash mixtures in the HTO facility. The solubility is characterized by the sulfur capacity, defined as:

$$C_s = (\text{wt \% S})\,(PO_2/PS_2)^{1/2}$$

where: C_s = sulfur capacity
wt % S = percent sulfur in coal
PO_2 = oxygen partial pressure
PS_2 = Gaseous sulfur species partial pressure

Figure 1-10 shows results for a number of slag mixtures.

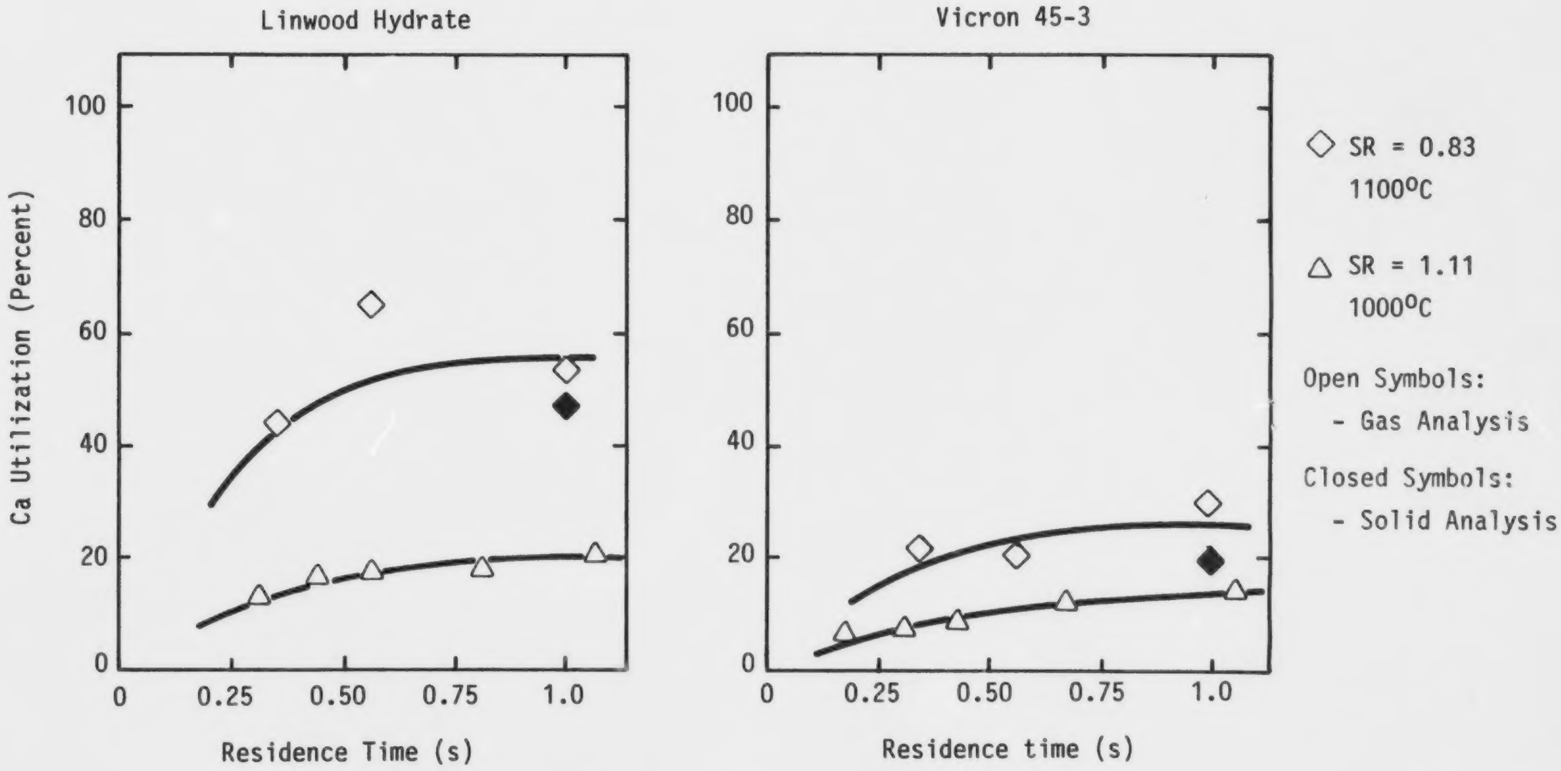


Figure 1-5. Calcium utilization in the ITR under fuel-rich and fuel-lean conditions for both Linwood atmospheric hydrate and Vicron 45-3 limestone.

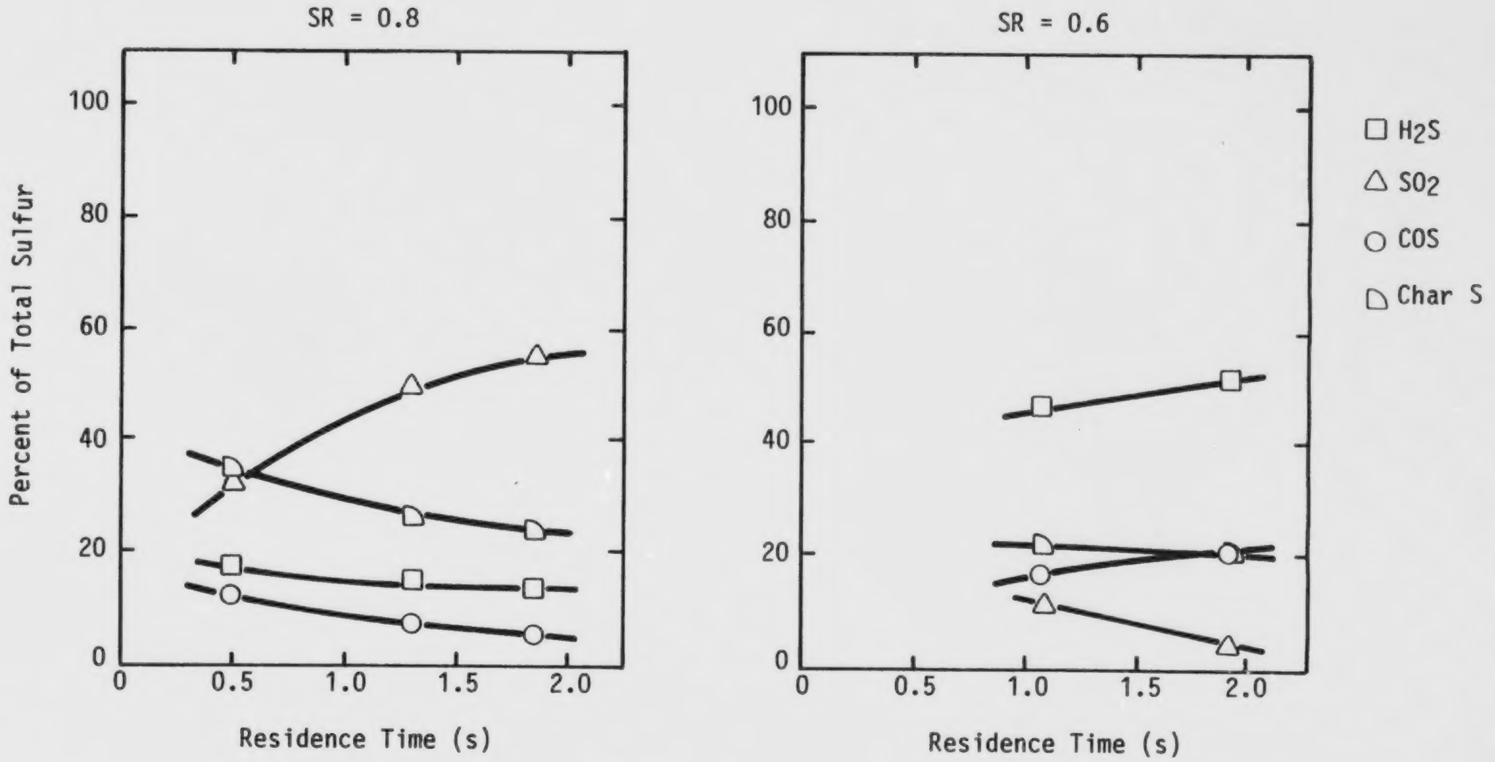


Figure 1-6. Sulfur speciation in the CTT firing Illinois coal at 17.6 kW (60,000 Btu/hr).

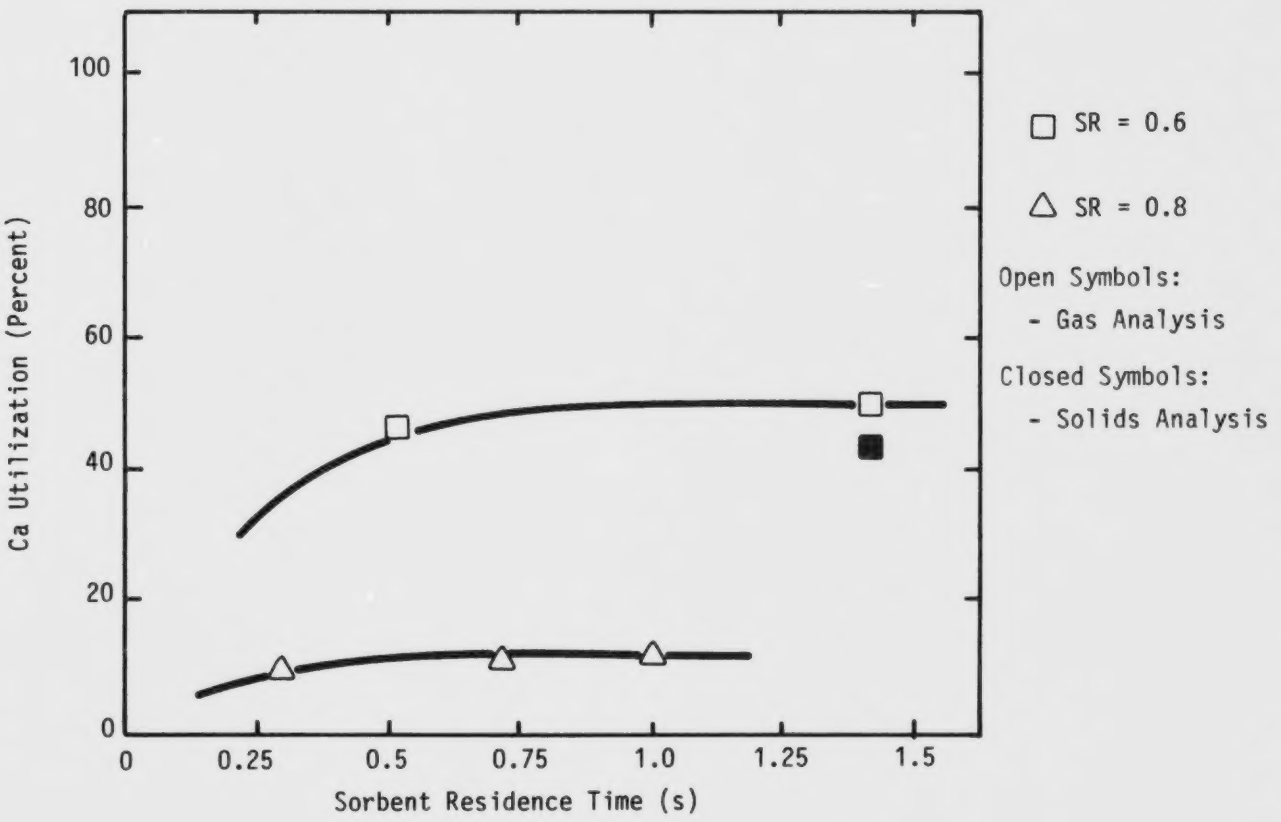


Figure 1-7. Calcium utilization in the CTT firing Illinois coal at 17.6 kW (60,000 Btu/hr), injecting Linwood atmospheric hydrate at about Ca/S = 1.0.

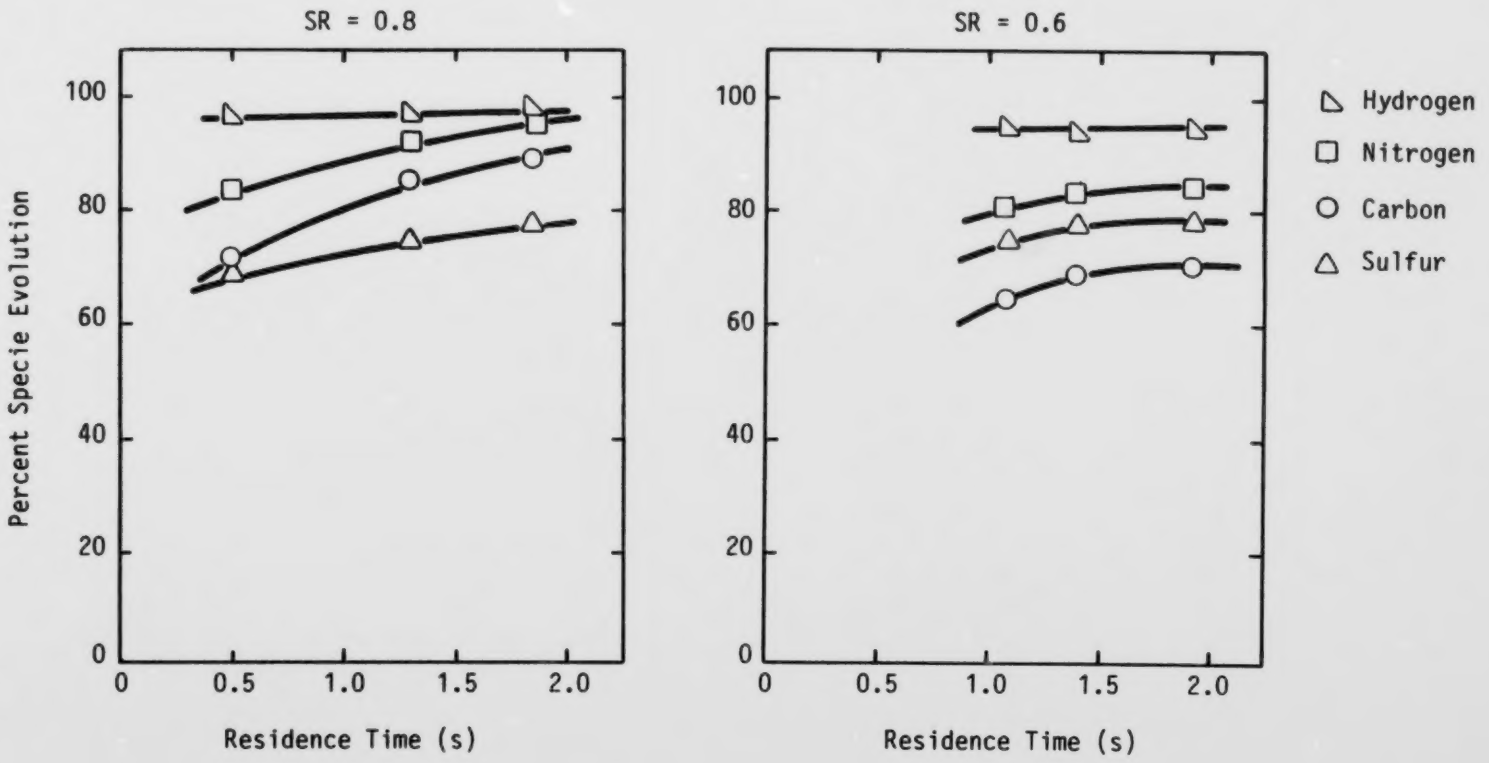


Figure 1-8. Species evolution from Illinois coal in the CTT at 17.6 kW (60,000 Btu/hr).

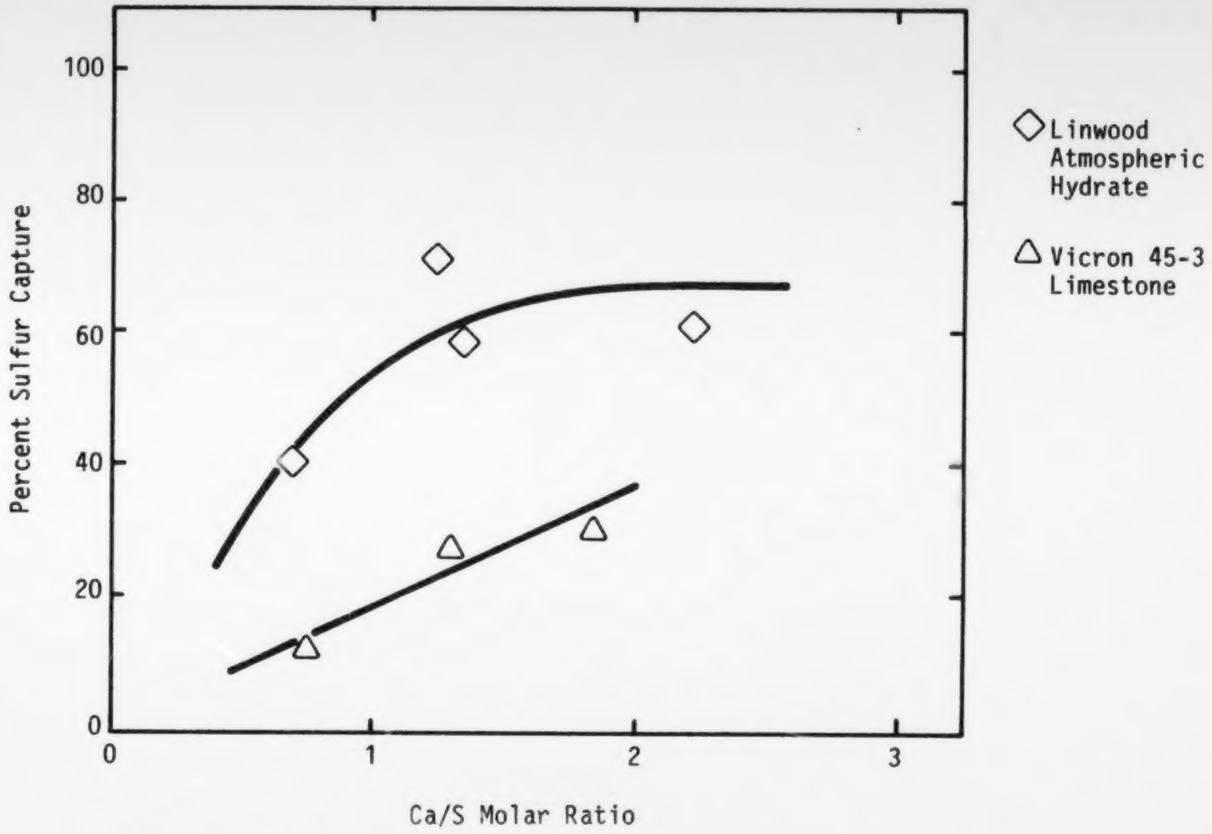


Figure 1-9. Capture of total sulfur in the CTT by the injection of sorbents when firing Illinois coal at 23.4 kW (80,000 Btu/hr), SR = 0.6. Both sulfur capture and Ca/S calculated based on the total input sulfur.

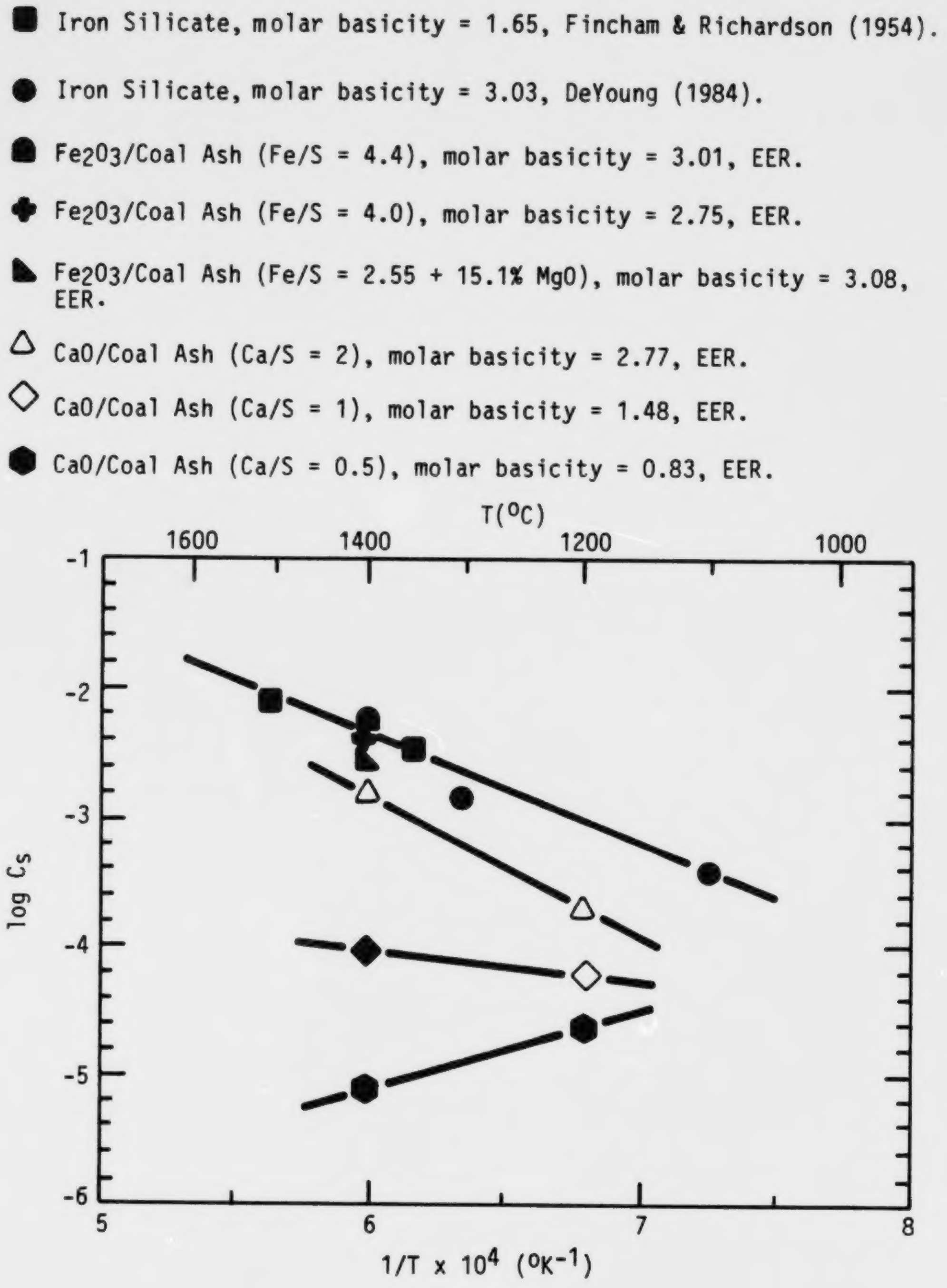


Figure 1-10. Influence of temperature and molar basicity on sulfur capacity for several slag mixtures (solid symbols - melted, open symbols - not melted).

These slag equilibrium values can be used along with gas phase equilibria and a sulfur mass balance to predict the best possible capture due to sulfur solubility of the slag. Figures 1-11 and 1-12 show examples of these best case equilibrium calculations. It is evident that calcium-based slags are not very soluble to sulfur and are of limited value in a slagging system due to the resulting rise in the mixture fusion temperature.

Iron-based slags are much more soluble to sulfur but only when unacceptably large quantities of iron is added. Also, the kinetics of the gas-slag sulfur capture process for iron-based slags have been shown to be slow by other researchers.

What the results of Figures 1-11 and 1-12 suggest is that: 1) large amounts of calcium in the slag can produce non-fluid slag mixtures at typical precombustor temperatures, and 2) the CaS that forms in the entrained flow portion of the reactor will tend to regenerate sulfur as the CaS dissolves into the slag.

Figure 1-13 shows the impact of CaO addition to Illinois coal ash on fluid temperature under both oxidizing and reducing conditions. For this high sulfur coal, an addition of CaO in excess of Ca/S = 1 causes a sharp increase in slag fluid temperature.

Fluxing additives such as P_2O_5, Fe_2O_3, CaF_2 and B_2O_3 were added in small quantities to CaO/ash slag mixtures corresponding to Ca/S = 1 and Ca/S = 2. Figure 1-14 shows that B_2O_3 was the most effective fluxing agent under reducing conditions.

To identify how quickly sulfur regenerates from slag when present at levels in excess of equilibrium, CaO was replaced with pure CaS and the rate of sulfur loss was measured. Figure 1-15 shows the relative rates of sulfur regeneration for a number of slag mixtures. In general, the higher the slag sulfur capacity and the higher the slag fluid temperature the slower the sulfur regeneration.

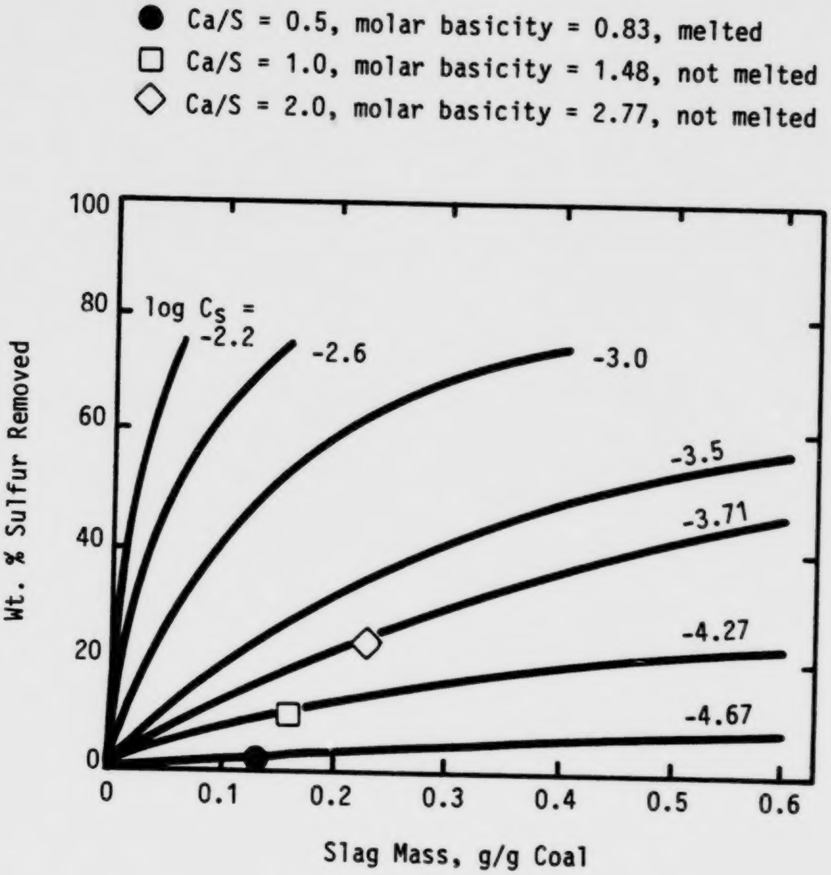


Figure 1-11. Equilibrium sulfur removal by slag for SR=0.5, T=1200°C, and an Illinois coal with 3.97% sulfur.

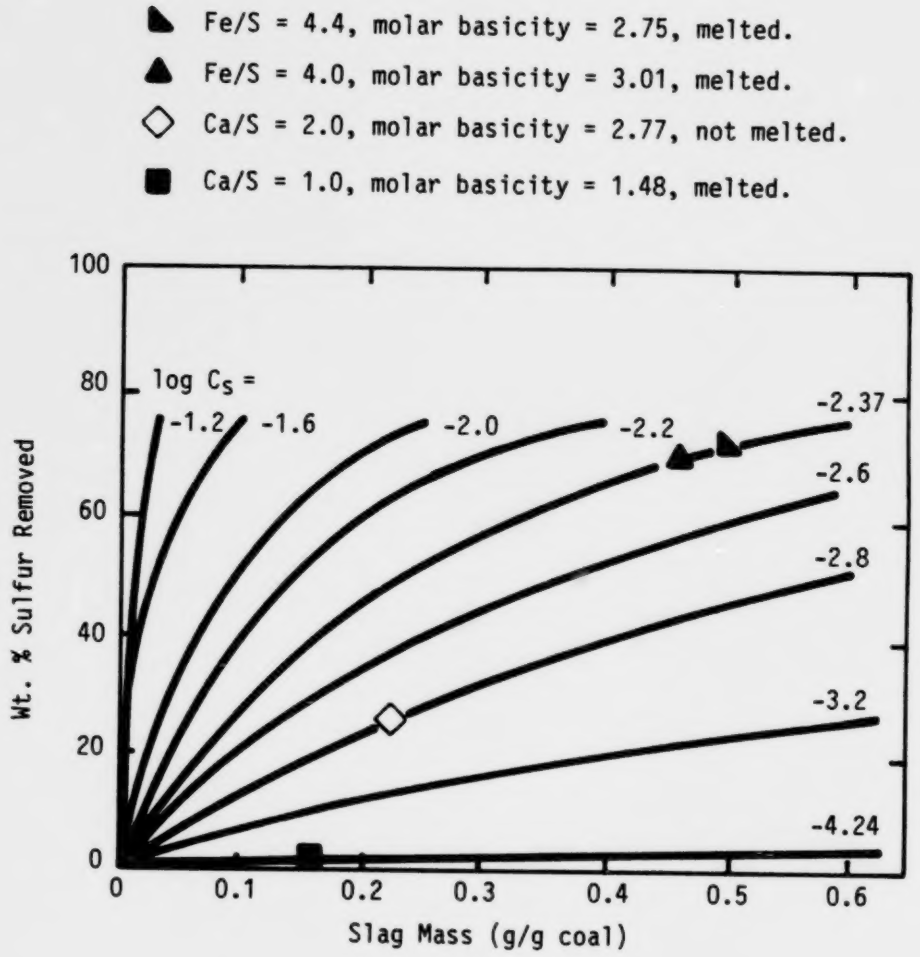


Figure 1-12. Equilibrium sulfur removal by slag for SR=0.5, T=1400°C, and an Illinois coal with 3.97% sulfur.

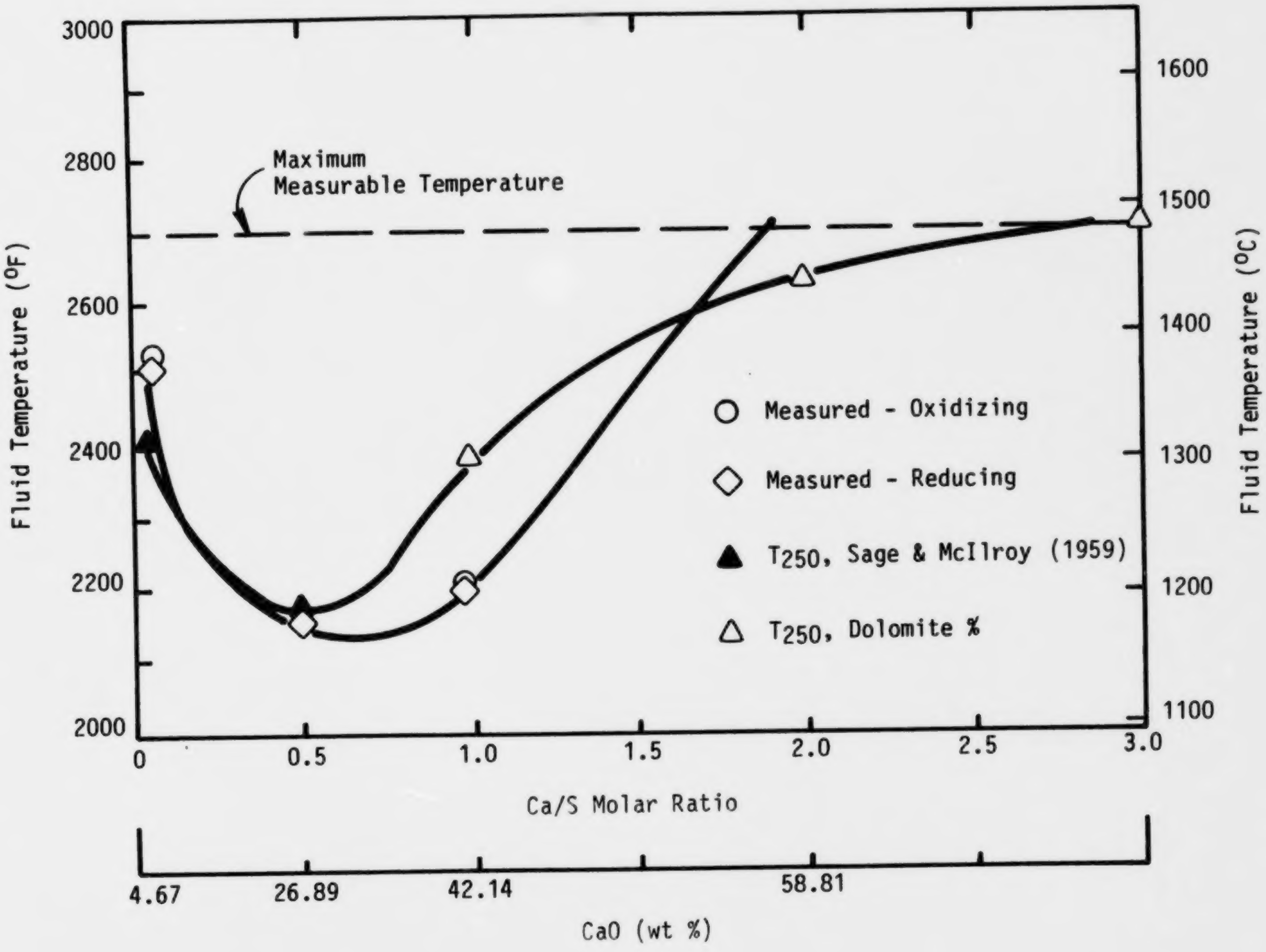


Figure 1-13. Fluid and T_{250} temperatures for Illinois coal ash/CaO mixtures.

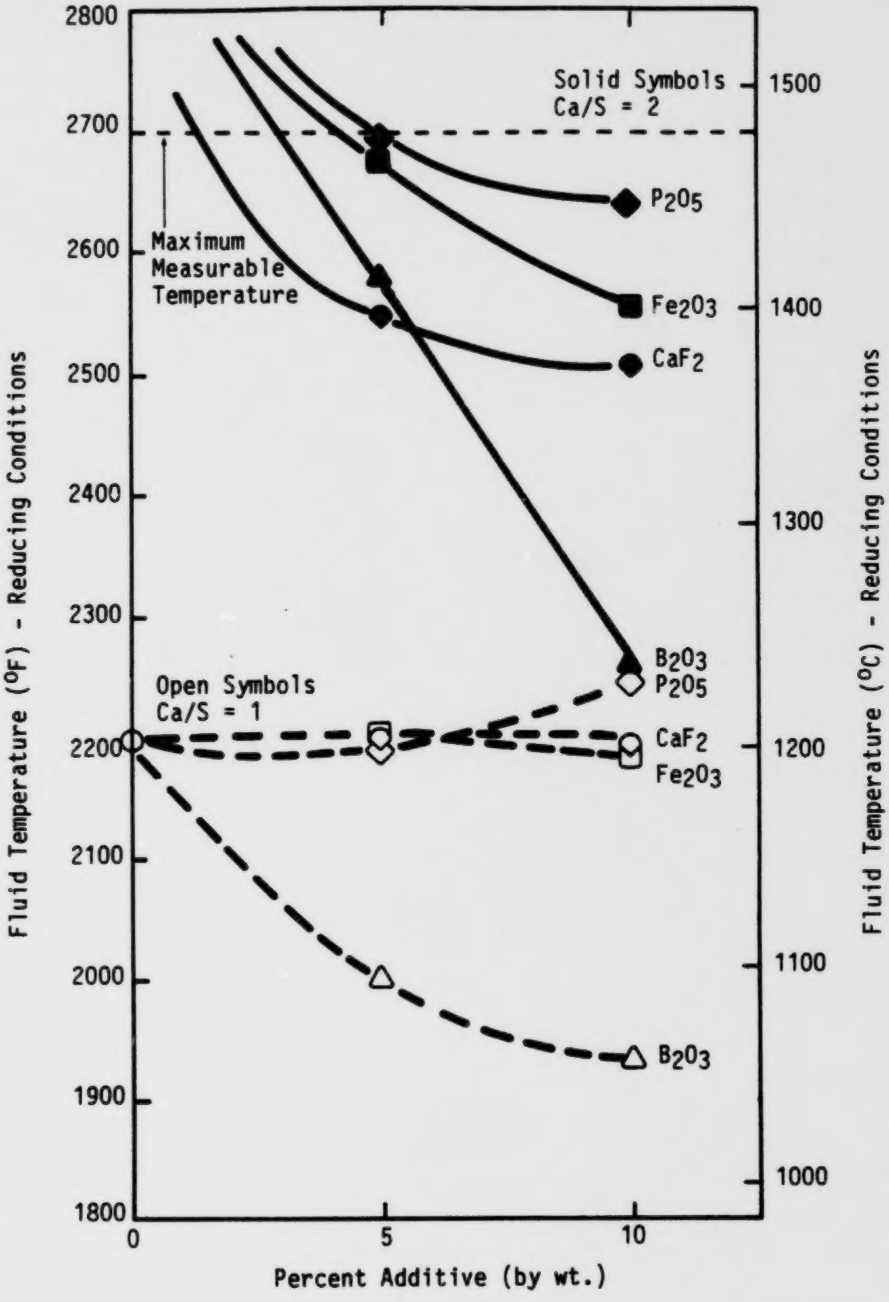


Figure 1-14. Influence of fluxing additives on the reducing fluid temperature of Illinois coal ash and CaO mixtures (open symbols correspond to Ca/S = 1 mixtures while solid symbols represent Ca/S = 2 mixtures).

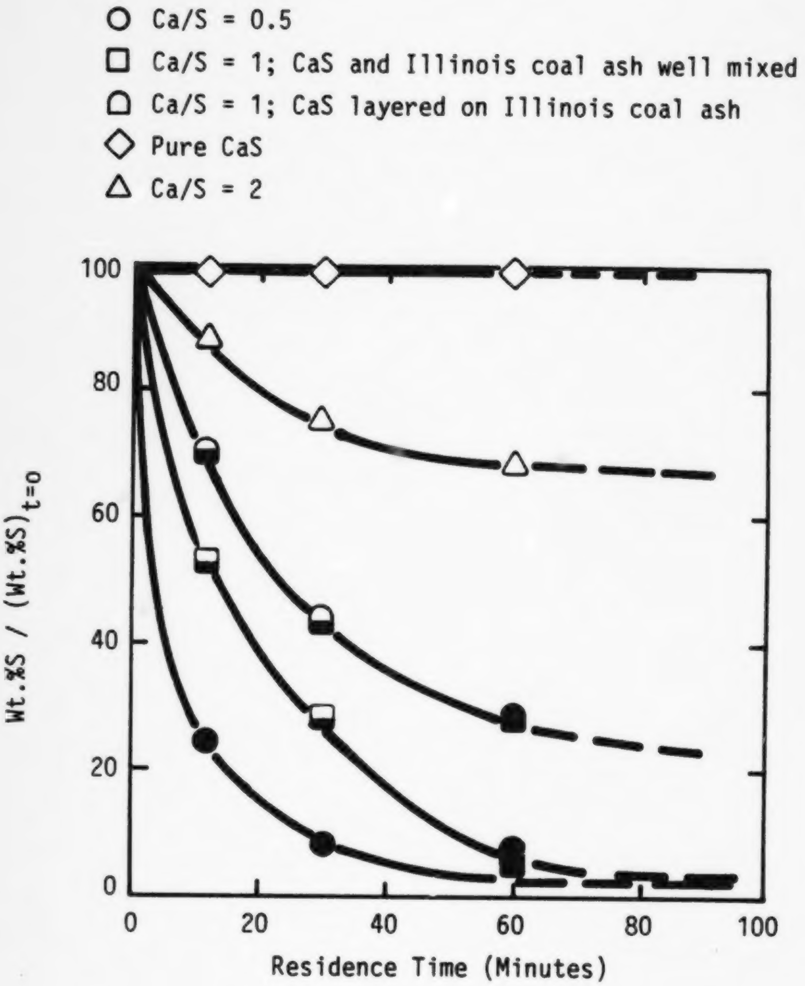


Figure 1-15. Desulfurization of CaS and Illinois coal ash slag mixtures, showing the influence of calcium content and mixedness (open symbols represent completely unmelted samples, solid symbols correspond to completely melted samples).

1.5 Conclusions

The scope of this program was focused on the area of fuel-rich sulfur capture since little more than theoretical predictions and a few uncertain test results were available. Several obstacles face the successful use of calcitic sorbents in fuel-rich coal-fired precombustors. The most important issues were investigated in this program, including: extent of entrained flow sulfidation, the speciation of sulfur as it evolves from coal under fuel-rich conditions, the equilibrium solubility of sulfur in molten slags, the impact of fluxing additives on slag fluidity and sulfur solubility, and the rate in which sulfur regenerates from slags containing a super-equilibrium level of sulfur.

The major conclusions from this program are summarized below:

- The sulfidation reactions between CaO and H_2S or COS are fast and under optimum conditions can capture a majority of the gas phase sulfur in a fuel-rich precombustor.
- The conditions which favor fuel-rich sulfur capture (deep substoichiometric operation and moderate temperatures) can result in poor carbon burnout and low slag fluidity.
- Typical molten coal ash and mixtures of coal ash and CaO are incapable of holding large amounts of sulfur in a coal precombustor environment when at equilibrium.
- Coal ash/CaO slags quickly desulfurize from super-equilibrium levels of sulfur at typical precombustor temperatures and gas compositions, indicating that rapid slag drainage designs are required.
- Slag fluxing additives, such as B_2O_3, can extend operating conditions which will make fuel rich sulfur removal a possibility over a wider range of coal types and precombustor systems.

Future work at large scale is now required to determine the practical limitations of sulfur capture in systems that have been tested and optimized for maximum ash rejection, continuous slag drainage, and minimal NO_x emissions. The results of this program provide a major portion of the necessary background information before proceeding in the final development of a precombustor system that can simultaneously control ash, NO_x and SO_x emissions.

2.0 INTRODUCTION

2.1 Precombustor Concept

Conversion of gas- and oil-fired combustion systems to coal firing is made difficult by the presence of mineral matter, nitrogen and sulfur in coal. Not only are fly ash emissions a health hazard, but the presence of mineral matter can impair operation of equipment that has not been designed for coal use. Deposition on heat transfer surfaces can cause reduced efficiency and increased corrosion and erosion. Nitrogen and sulfur in coal can be released into the environment as NO_x and SO_x, which are both precursors of acid rain. Cost of precleaning coal or post-combustion clean-up are prohibitively expensive in most applications at this time.

One concept which offers the potential for simultaneous removal of ash and reduction of NO_x and SO_x emissions at the burner prior to a boiler or heater furnace is coal-fired precombustion. A precombustor burns coal in a chamber exterior to the normal furnace region (see Figure 2-1). Mineral matter in the coal (that does not vaporize) can be separated from the exhaust gases aerodynamically and drained as molten slag from the precombustor. Ash separation over 90 percent has been reported from existing systems. Operation under staged combustion conditions (i.e., fuel-rich in the precombustor with fuel-lean burnout in the retrofitted furnace) has been shown to reduce NO_x emissions by over 60 percent. Research efforts at Energy and Environmental Research Corporation (EER) (La Fond and Payne, 1985) and elsewhere (Dykema, 1985; LeCrew and White, 1985; Mattsson and Stankevics, 1985; and Zauderer and Fujimura, 1985) have been directed at developing precombustor systems which optimize ash separation and NO_x reduction.

This program was directed at the key issue that has not been adequately addressed by previous research--whether sulfur can be controlled internally in precombustor systems.

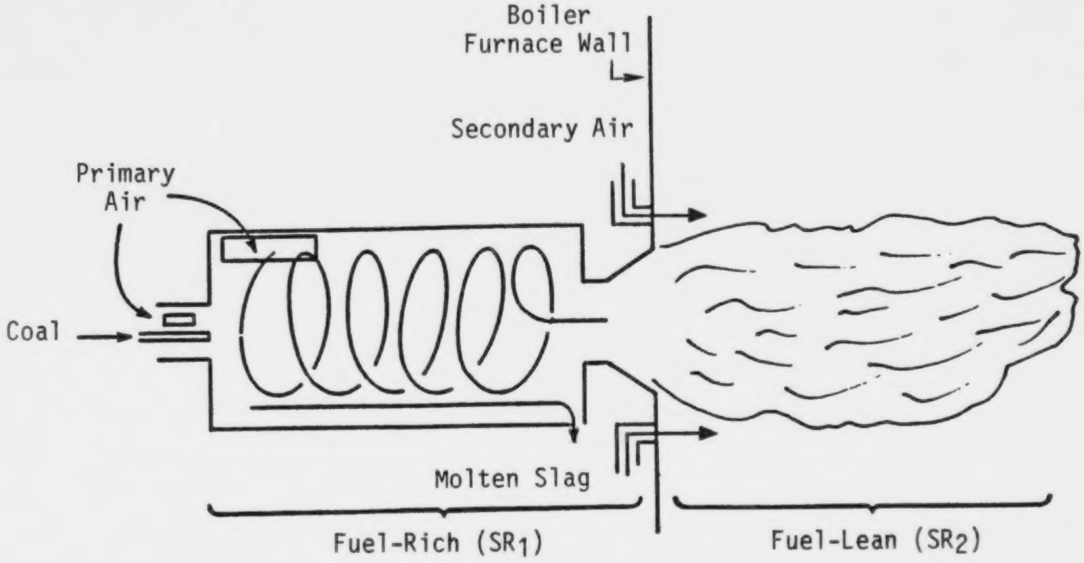

Boiler
Furnace Wall
Secondary Air
Primary
Air
Coal
Molten Slag
Fuel-Rich (SR_1)
Fuel-Lean (SR_2)

Figure 2-1. Common cyclonic precombustor in staged combustion configuration attached to boiler furnace wall.

2.2 Sulfur Control

In recent years, much attention has been given to the use of calcium-based sorbents (calcitic and dolomitic carbonates and hydrates) for the removal of gas phase SO_2 by reaction with CaO to form $CaSO_3$ or $CaSO_4$. Thermodynamically, sulfur is more stable as CaS under fuel-rich conditions than $CaSO_4$ in a fuel-lean environment. Figure 2-2 shows the effect of stoichiometry and temperature on equilibrium solid calcium-sulfur compounds for a Pittsburgh coal. Under fuel-rich conditions CaS formation is favored and is thermodynamically stable even at fairly high combustion temperatures. Under fuel-lean conditions $CaSO_4$ is the favored species; however, above approximately 1300°C (2372°F), $CaSO_4$ is not thermodynamically stable. Figure 2-3 presents data by Silcox et al. (1986) that shows the sharp drop in calcium utilization as the reactor temperature was raised from 1150°C (2102°F) to 1300°C (2372°F). Figure 2-2 also shows that the stability of either solid sulfur species is low at conditions slightly below stoichiometric.

The reactions that take place to form CaS under substoichiometric conditions include:

$$CaO + H_2S \longrightarrow CaS + H_2O.$$

$$CaO + COS \longrightarrow CaS + CO_2.$$

Borgwardt et al. (1984) have shown that the kinetics of the H_2S and COS reactions are faster than the fuel-lean sulfur reaction of:

$$CaO + SO_2 + 1/2\ O_2 \longrightarrow CaSO_4.$$

Borgwardt's studies were performed in a laboratory scale system under ideal conditions and low temperatures. The concept has been extended to testing in pilot scale fuel-rich precombustor systems by various researchers with either unfavorable or unsubstantiated results.

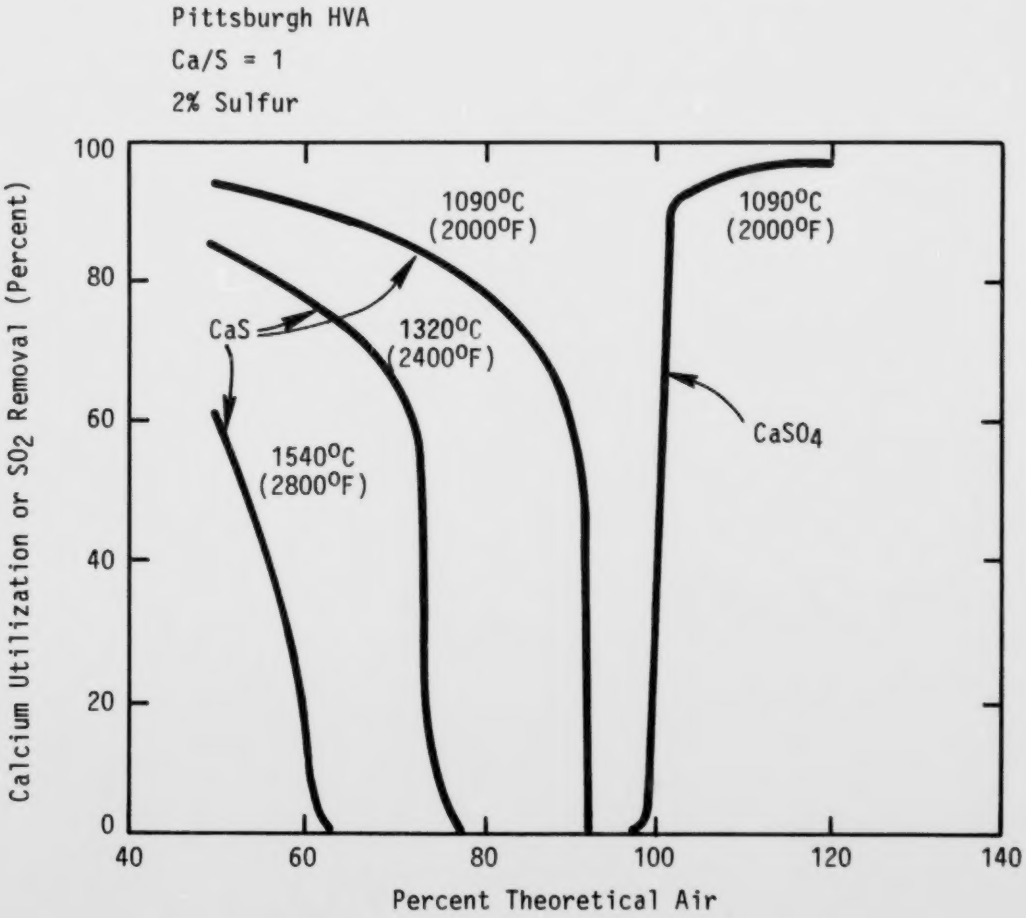


Figure 2-2. Equilibrium stability of solid calcium-sulfur compounds (England et al., 1986).

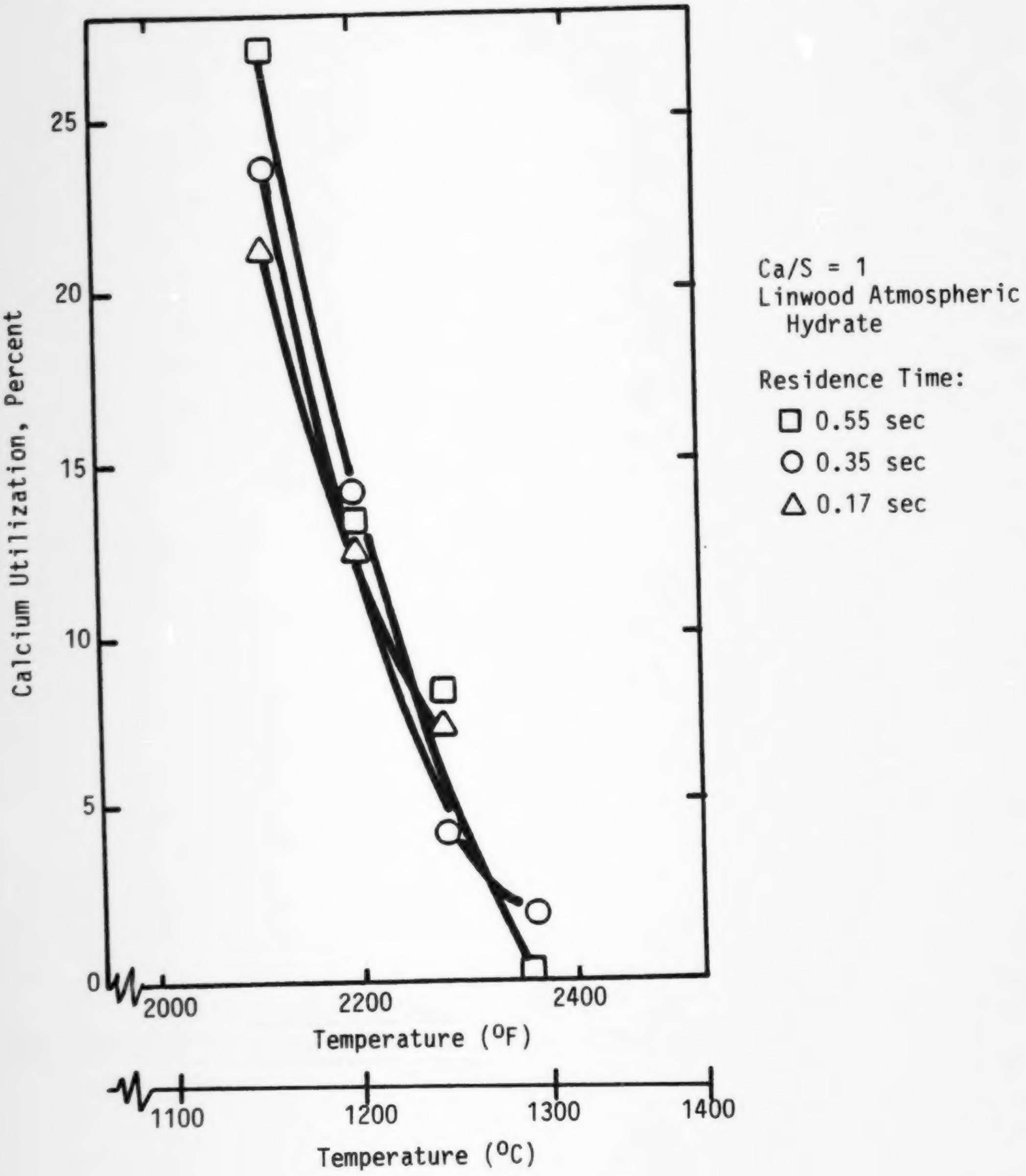


Figure 2-3. Calcium sulfate formation at elevated injection temperatures (Silcox et al., 1986).

The process of calcium-based sorbent injection into fuel-rich precombustors is a complicated sequence of coal pyrolysis and oxidation, sulfur species evolution, sorbent calcination, sulfidation and slag formation. Figure 2-4 shows schematically some of the important physical transformations that may be occurring within a fuel-rich precombustor system.

Upon injection, the solids are in an entrained flow phase. Coal enters the precombustion chamber and begins to pyrolyse, giving off volatiles, sulfur and nitrogen compounds and forming char. The coal in various stages of pyrolysis may reach a wall where it can continue to devolatilize or possibly become encapsulated in a liquid slag layer. At the same time, if sorbent material such as limestone ($CaCO_3$) or calcium hydroxide ($Ca(OH)_2$) is injected into the chamber for the purpose of sulfur removal, CO_2 or H_2O is driven off the sorbent to form CaO where it can react with sulfur compounds in the gas phase. The calcium-sulfur solids that are formed (CaS under strongly fuel-rich conditions) can reach the slag covered precombustor walls and be flushed out of the system through the slag drain or regenerate sulfur back into the gas phase. The calcined sorbent can also reach the slag layer without completely reacting where it can continue to react with gas phase sulfur, combine with liquid phase sulfur, or become deactivated by interaction with mineral matter.

Successful application of sulfur control in fuel-rich precombustors will depend on better understanding of the following key issues:

- Required conditions for sulfidation of calcium-based sorbents;
- Compatability of sulfidation conditions to practical requirements of precombustors, such as carbon burnout and slag fluidity;
- Means of removal of sulfur bearing solids, including sulfur solubility and stability in coal ash slag; and
- Impact of additives on altering or extending operating conditions to reach all performance goals simultaneously.

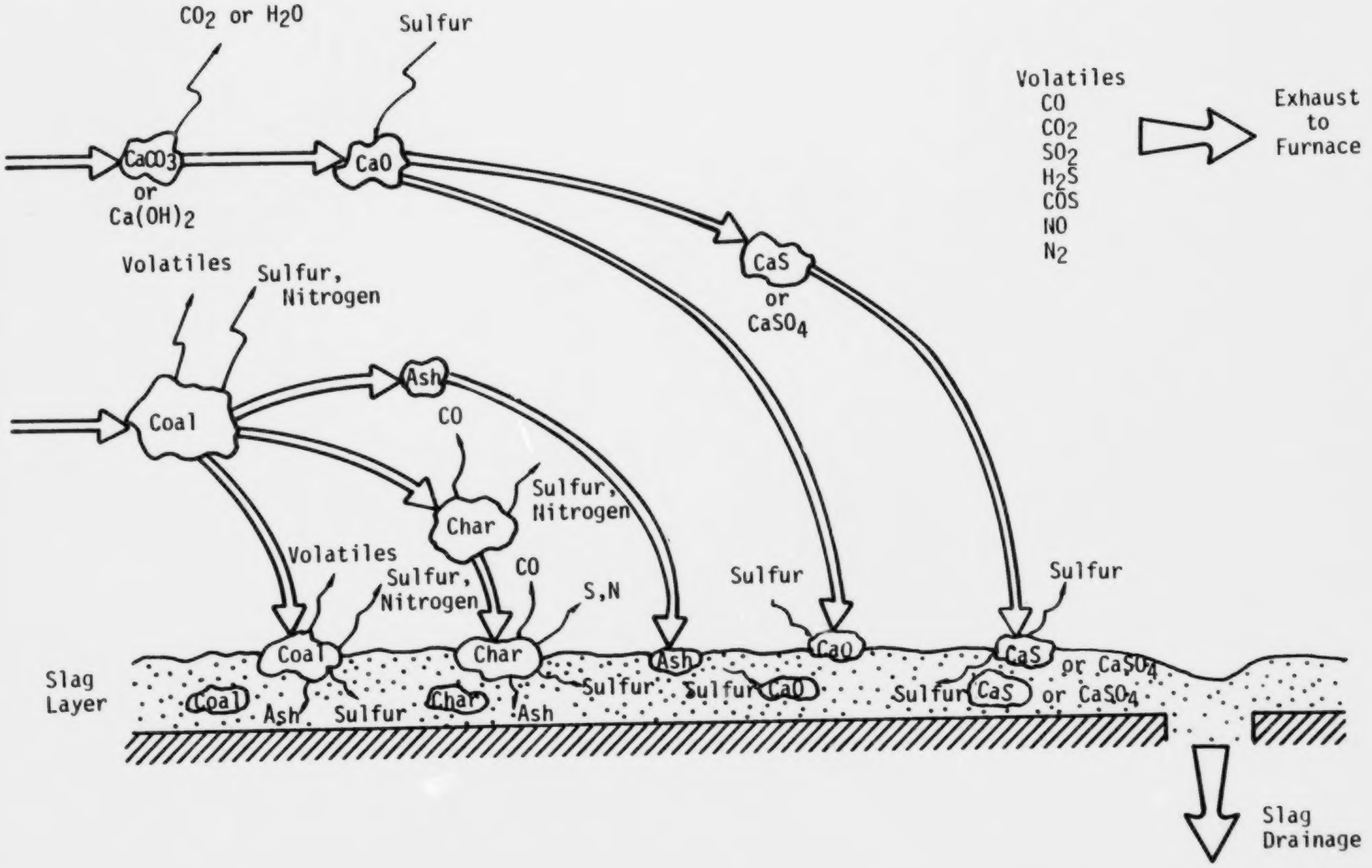

CO2 or H2O
Sulfur
CaCO3
or
Ca(OH)2
CaO
CaS
or
CaSO4
Volatiles
CO
CO2
SO2
H2S
COS
NO
N2
Exhaust
to
Furnace
Volatiles
Sulfur,
Nitrogen
Coal
Ash
CO
Char
Sulfur,
Nitrogen
Volatiles
Sulfur,
Nitrogen
CO
S,N
Sulfur
Sulfur
Coal
Char
Ash
CaO
CaS
or CaSO4
Slag
Layer
Coal
Ash
Sulfur
Char
Ash
Sulfur
Sulfur
CaO
Sulfur
CaS
or CaSO4
Slag
Drainage

Figure 2-4. Schematic diagram of some of the important mechanisms occuring in a fuel-rich precombustor system with sorbent addition.

2.3 Program History

This program was organized in two phases. Phase I included a review of available literature on fuel-rich sulfur capture and cyclonic coal combustors and design and testing of a 293 kW (1 x 10^6 Btu/hr) coal-fired precombustor. The precombustor was designed based on previous experience with low-NO_x systems and the literature review. It was tested on EER's fire tube package boiler simulator facility to establish conditions which favored simultaneous control of NO_x, SO_x, and particulate matter and to identify areas that required further investigation.

The Phase I work was carried out under the direction of EPA's LIMB Branch, with Chuck Masser serving as Project Officer. A summary of the results of the Phase I work can be found in the background portion of this report (Section 3.0).

Although the Phase I testing showed some evidence of fuel-rich sulfur capture and provided valuable design and operational experience, the scale of the test apparatus along with sampling, analysis and operational difficulties limited the amount of useful information that could be generated.

The Phase I testing led to the formulation of a second phase test plan, which is the prime topic of this final report. The Phase II testing was structured to investigate a broader range of issues in smaller, well-controlled experimental facilities in order to generate a more complete set of basic precombustor design data. The Phase II efforts were directed by EPA's Combustion Research Branch, with Joe McSorley serving as Project Officer.

3.0 BACKGROUND

There were three main sources of information that provided background information before commencement of Phase II of this program: 1) testing experience on the Phase I pilot-scale precombustor system and EER's Vortex Containment Combustor (VCC); 2) review of information available from the steel and glass industries on sulfur solubility in slags and slag fluxing additives; and 3) literature review of fundamental research on the subject of calcium sulfidation.

3.1 Precombustor Experience

As mentioned earlier, Phase I of this program involved construction and testing of a precombustor system. The testing was exploratory in nature, but provided enough information to structure more detailed measurements in Phase II. The Phase I tests focused on screening the effects of operational parameters on sulfur capture by sorbent injection under fuel-rich conditions. At the same time, the reduction of NO_x and particulate emissions was monitored to establish operating conditions for simultaneous control of all three pollutants. Parameters varied were the first stage stoichiometric ratio (SR_1), type of sorbent, type of fuel, and method of primary air injection (axial vs. tangential). Sorbent enhancement by addition of a small amount of Fe_2O_3 was also tested. The furnace configuration was modified to add slag baffles at the end of the precombustor for improved solids rejection.

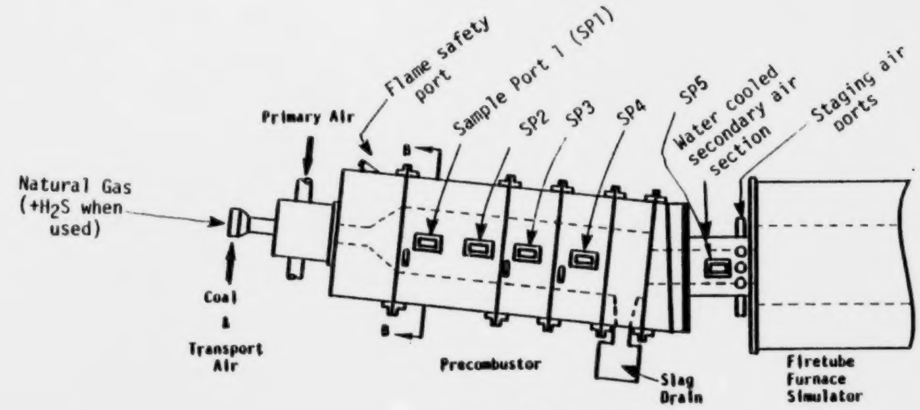
The concept of sulfur capture in fuel-rich precombustors was first suggested by work done at EER by Case et al. (1985) that indicated that improved sulfur capture may occur in the fuel-rich environments found under low-NO_x combustion conditions. There were also three theoretical factors that suggested improved sulfur capture under fuel-rich conditions compared to fuel-lean conditions. First, lower fuel-rich flame temperatures could reduce sintering of the sorbent surface, thus increasing sorbent reactivity for sulfidation reactions. Second, by forming calcium sulfide (CaS) under reducing conditions rather than calcium sulfate ($CaSO_4$), the internal pore blockage which hinders sulfation reactions is reduced, allowing free diffusion of H_2S and COS into the heart of the CaO particles. And third, CaS is thermodynamically more stable under fuel-rich conditions at combustion temperatures than $CaSO_4$ under fuel-lean conditions.

In practice, potential difficulties in achieving high sulfur capture under fuel-rich conditions include: 1) the oxidation of CaS to form CaO and SO_2 if exposed to a hot fuel-lean environment, 2) the ability to reject ash in either a dry or molten form while simultaneously obtaining both high carbon burnout and high sorbent reactivity in a precombustor system, and 3) regeneration of sulfur from molten ash/CaS mixtures.

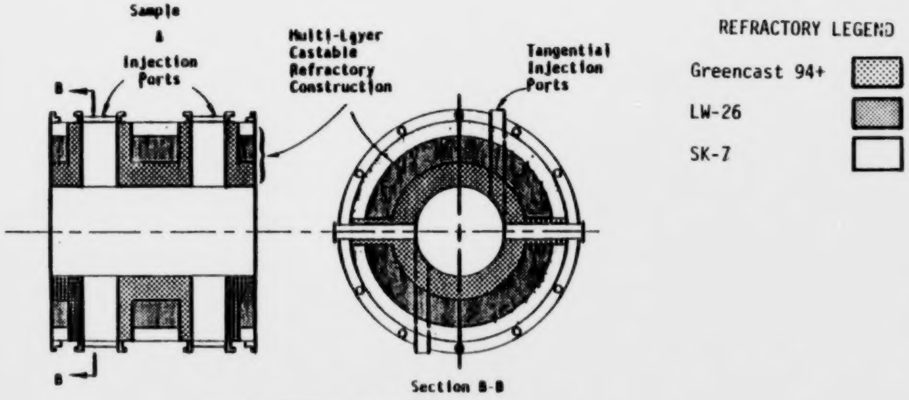
A sketch of the precombustor system tested in Phase I is presented in Figure 3-1. The precombustor was designed to fire with either axial or tangential primary air injection and could accommodate baffles at the precombustor exit to increase slag rejection.

Initial characterization of the system included temperature profiling within the fuel-rich and fuel-lean zones of the system. Figure 3-2 presents the profile measured at a stoichiometric ratio of 0.5. Estimated temperatures at varying first stage stoichiometry (based on adiabatic flame temperatures and calculated heat loss) were used to calculate equilibrium sulfur speciation with and without sorbent addition. The results of these equilibrium computations are presented in Figure 3-3. These plots suggest that conditions which favor H_2S formation are favorable for calcium sulfidation. Conversion to CaS is favored at stoichiometric ratios of 0.6 or less and improves at lower temperatures.

NO_x emissions were measured as a function of first stage stoichiometric ratio (SR_1). Measurements were made for SR_1 between 0.5 and 0.9, holding the overall stoichiometric ratio (SR_T) constant at 1.2. Emissions from both natural gas- and Illinois coal-firing were measured and are presented in Figure 3-4. The natural gas NO_x levels were below 100 ppm for every case. The NO_x emissions for the coal-fired runs were below 115 ppm for SR_1 between 0.6 and 0.8. Fine tuning of the precombustor and second stage air injection


Natural Gas (+H2S when used)
Coal & Transport Air
Primary Air
Flame safety port
Sample Port 1 (SP1)
SP2
SP3
SP4
SP5
Water cooled secondary air section
Staging air ports
B
B
Precombustor
Slag Drain
Firetube Furnace Simulator

GENERAL ARRANGEMENT


Sample & Injection Ports
B
B
Multi-Layer Castable Refractory Construction
Tangential Injection Ports
Section B-B
REFRACTORY LEGEND
Greencast 94+
LW-26
SK-7

CROSS SECTION REFRACTORY DETAIL

Figure 3-1. Precombustor arrangement and refractory detail.

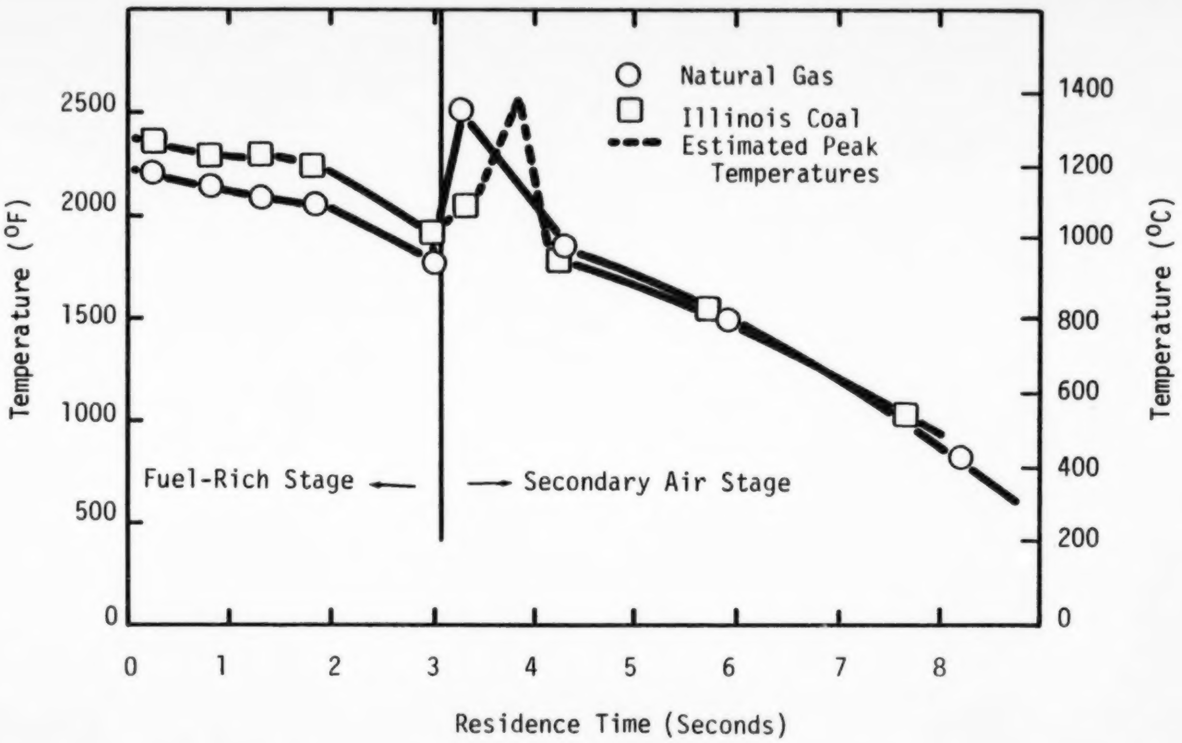
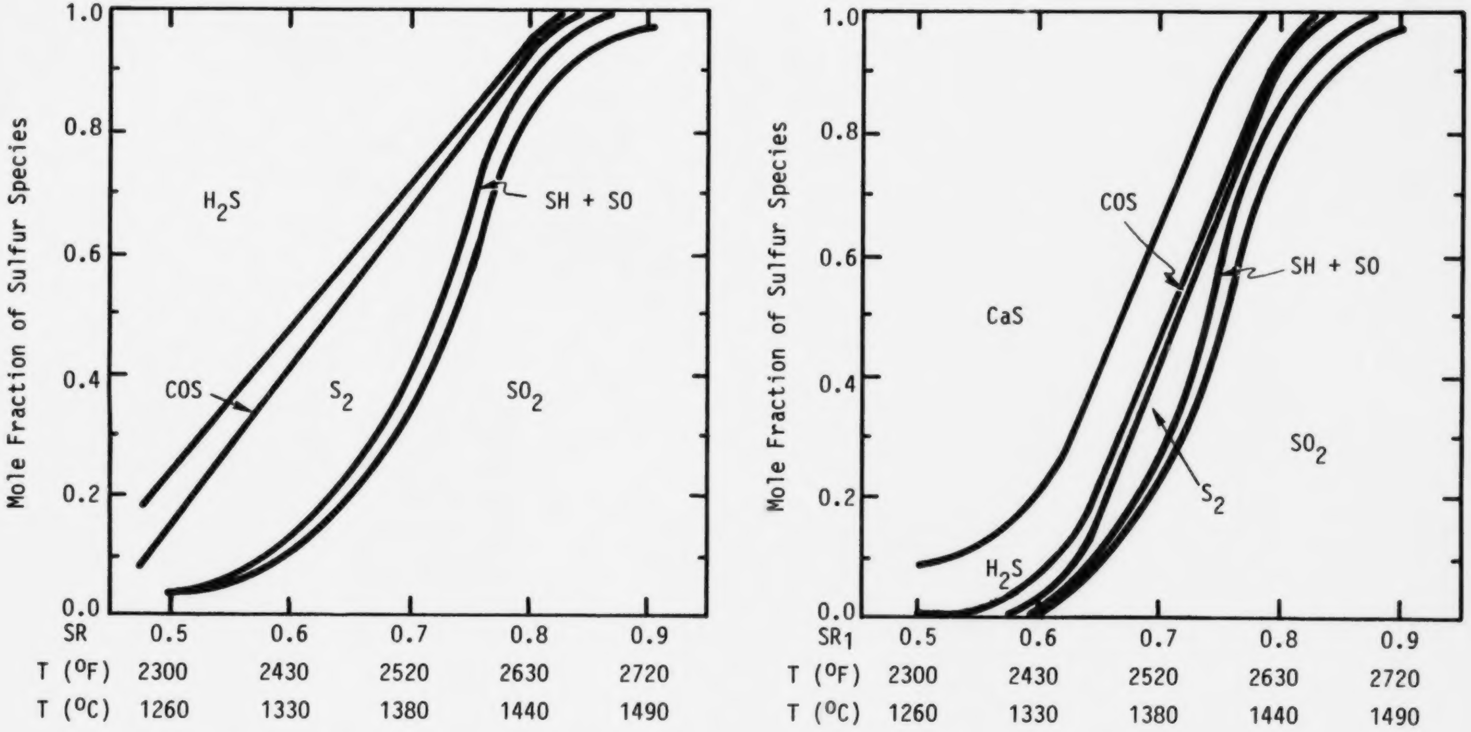


Figure 3-2. Mean gas temperatures and bulk residence times in the precombustor and furnace ($SR_1 = 0.5$, 0.3 MW_t).



(a) Illinois Coal Without $CaCO_3$ Input

(b) Illinois Coal With $CaCO_3$ Input (Ca/S=2)

Figure 3-3. Equilibrium distribution of sulfur species under the reducing conditions of the precombustor for Illinois coal with and without calcium present.

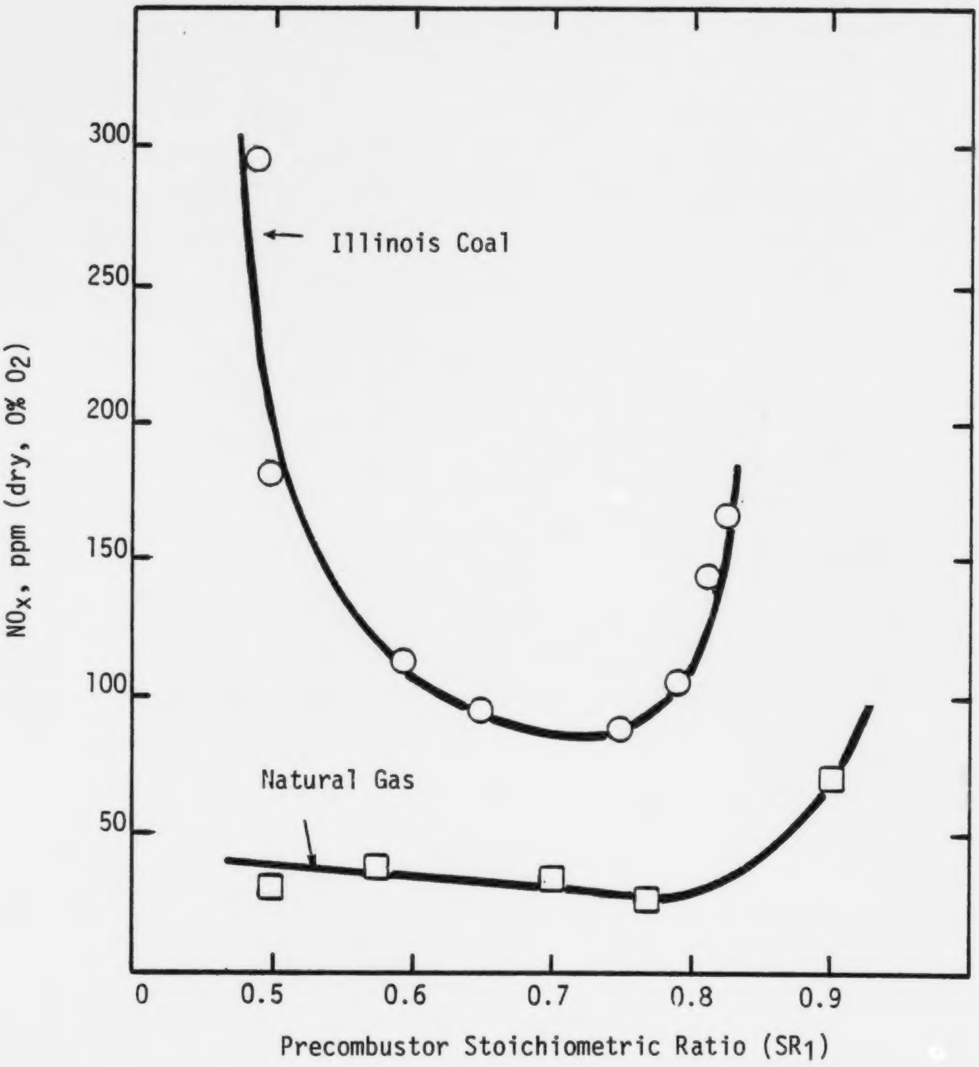


Figure 3-4. Stack NO_x emissions as a function of SR_1 for Illinois coal and natural gas ($SR_T = 1.2$).

could result in lower NO_x emissions over a broader range of first stage stoichiometric ratios.

The exposure of pulverized sorbent material to sulfur species under staged combustion conditions resulted in higher overall sulfur capture than when exposed solely to fuel-lean conditions. Figure 3-5 shows that injection of H_2S into the fuel-rich first stage with either Vicron 45-3 or dolomite gave higher overall exhaust SO_2 reductions than when SO_2 was injected into the fuel-lean second stage. The sorbent was injected along with the primary air for both cases to assure the same thermal environment and thus, similar sorbent reactivity. Although these tests showed that fuel-rich sulfur capture could potentially improve sorbent-based SO_2 reduction in a staged combustion system, they did not address such problems as loss or "regeneration" of sulfur species from calcium-sulfur compounds in the fuel-lean stage or differentiate between fuel-rich sulfidation and fuel-lean sulfation reactions.

Solids sampling from the exit of the fuel-rich precombustor provided important information that was masked by the previous measurements. A calcium utilization (sulfur capture at Ca/S = 1) of greater than 30 percent was measured for both natural gas/H_2S and Illinois coal flames using Vicron 45-3 as the sorbent. Assuming a linear increase in capture as the Ca/S ratio increases, this would correspond to sulfur capture levels of more than 60 percent at Ca/S = 2. However, gas phase SO_2 measurements made in the system exhaust indicated sulfur capture of only 20 and 25 percent under natural gas/ H_2S and coal firing, respectively, indicating that regeneration of sulfur species was occurring in the fuel-lean second stage. Results from the natural gas testing are shown in Figure 3-6. Analysis of the solids also indicated that under extremely rich first stage conditions (stoichiometric ratio of 0.5) the sulfur was captured as calcium sulfide (CaS), as expected.

The use of slag baffles to help retain solids in the precombustor resulted in rejection of 28 percent of the solids. As Figure 3-7 shows, an increase in sulfur capture was recorded when the slag baffles were in use indicating that some captured sulfur from the first stage (in the form of

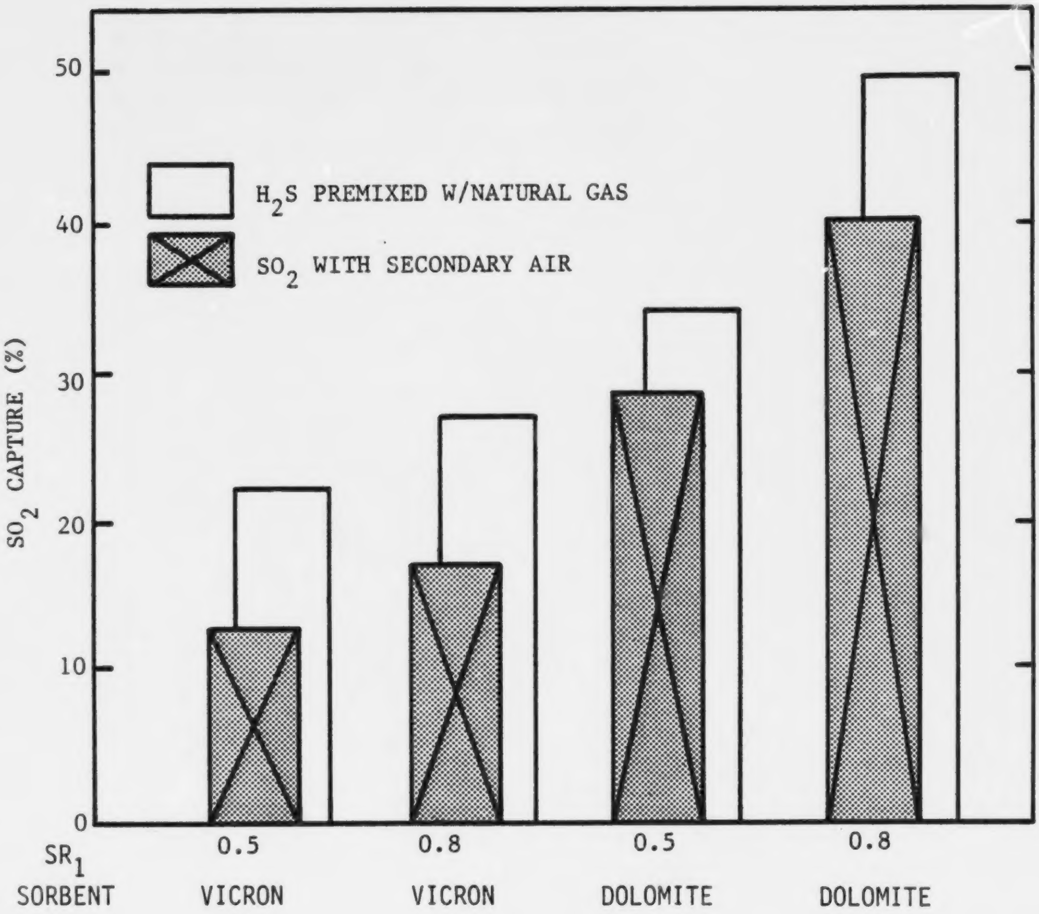


Figure 3-5. Sulfur capture when firing natural gas (0.3 MW_t) and injecting Vicron 45-3 and dolomite with the primary air at Ca/S = 2 (SR_T = 1.2).

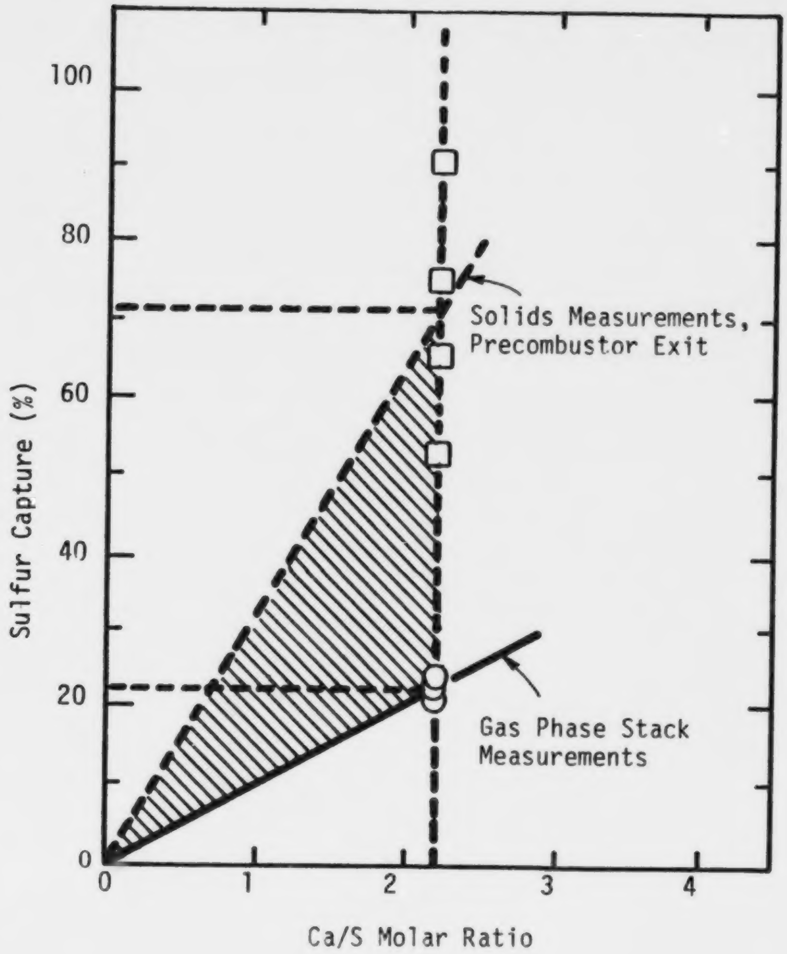
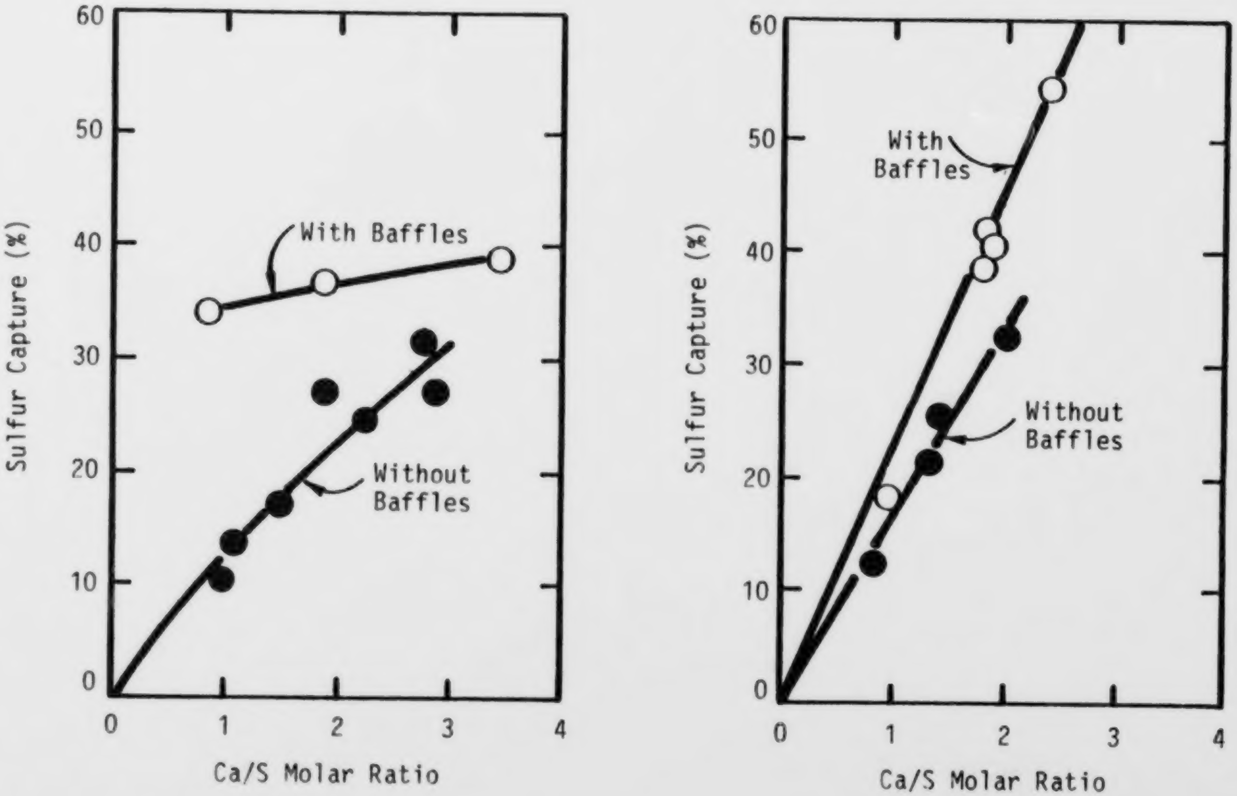


Figure 3-6. SO_2 capture based on gas phase stack measurements and potential SO_2 capture based on calcium utilization of solids samples. Vicron 45-3 in a fuel-rich natural gas/H_2S flame (SR_1 = 0.5, SR_T = 1.2, 0.3 MW_t).



(a) Natural Gas + H_2S

(b) Illinois Coal

Figure 3-7. Effect of increased solids removal on sulfur capture for two fuels. Vicron 45-3 injected with primary air (SR_1 = 0.5, 0.3 MW_t).

CaS) was indeed being lost to regeneration in the fuel-lean second stage. Also, the incremental increase in sulfur capture corresponded well to the expected capture level based on solids measurements of calcium utilization. The solids analyses for the coal-fired tests also indicated that a substantial portion of the exiting particles remained as char (carbon burnout of 61 to 69 percent at $SR_1 = 0.5$).

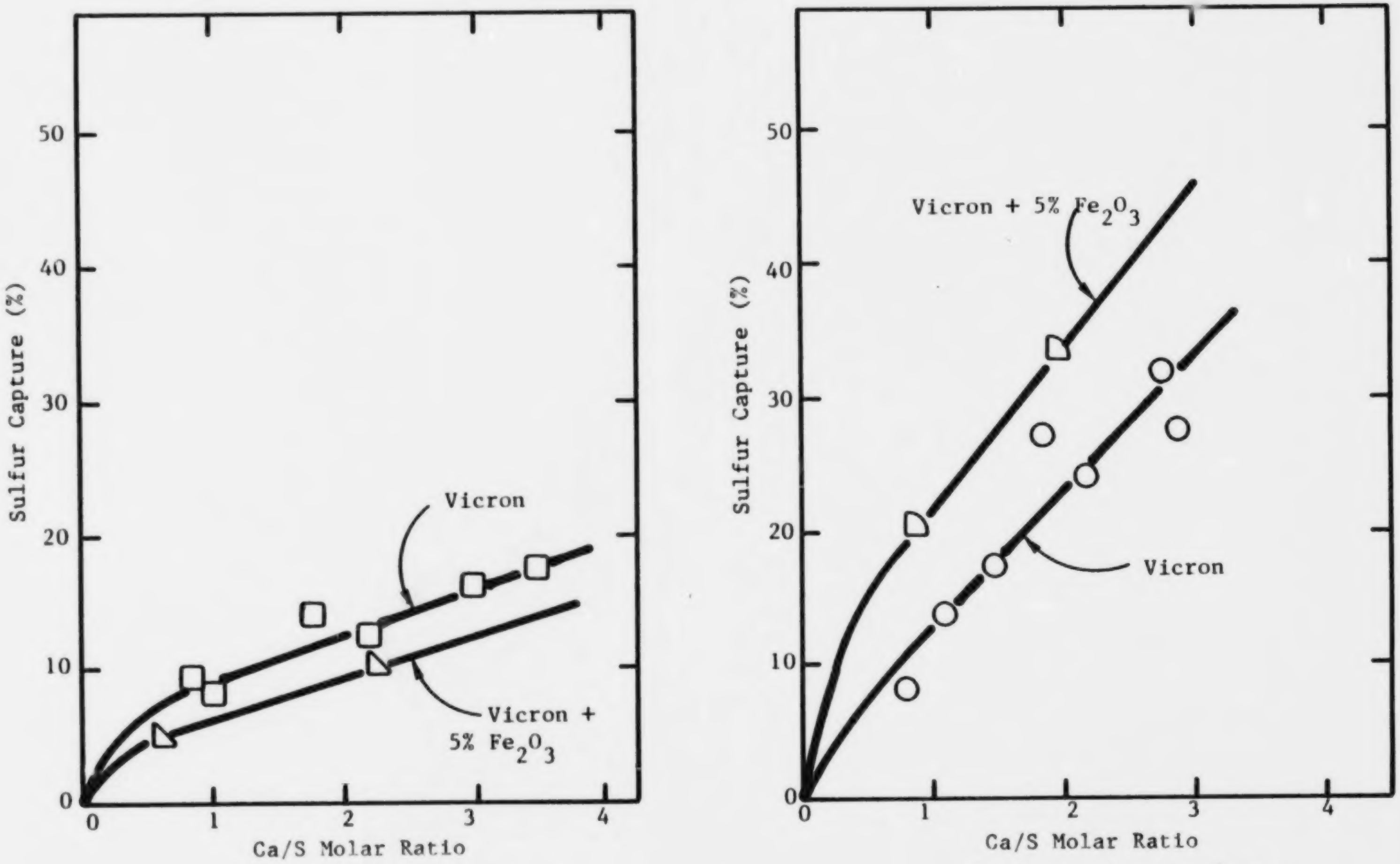
The addition of 5 percent by weight of iron oxide (Fe_2O_3) to the sorbent resulted in an improvement in overall sulfur capture from 24 percent to 34 percent at $Ca/S = 2$ for the natural gas/H_2S case (see Figure 3-8). This testing showed the potential of mineral matter additives for the enhancement of fuel-rich sulfur capture but was incapable of providing insight into the mechanisms of the sulfur capture process.

Other precombustor experience that impacted the formation of the Phase II work plan and interpretation of the results included testing of EER's Vortex Containment Combustor (VCC) (La Fond et al., 1985 and 1986). The VCC is an advanced cyclonic combustor which features:

- Reverse vortex flow for efficient particle separation.
- Long fuel residence times in an aerodynamic suspension.
- Selective ash rejection from the combustion zone.
- High radial velocity component of the inlet air to minimize wall deposition of ash and char.

As part of a Department of Energy program (Contract number: DE-AC22-85PC80256) the 0.9 MW_t (3×10^6 Btu/hr) precombustor shown in Figure 3-9 was tested under fuel-rich conditions for ash retention efficiency, NO_x reduction by staging and reburning, system pressure drop, slag drainage, carbon utilization, and SO_2 reduction.

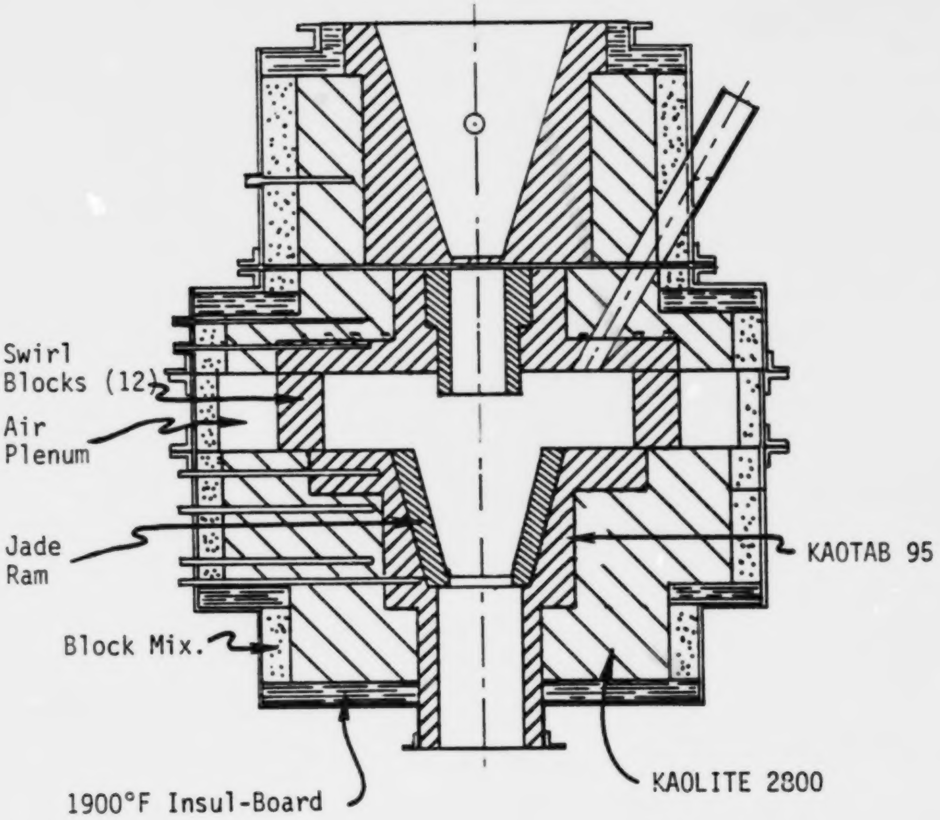
Figure 3-10 shows that over 80 percent of the coal ash could be separated from the exhaust stream over a wide range of firing rates and at low system pressure drops. NO_x was effectively controlled by over 60 percent



(a) SO_2 with secondary air

(b) H_2S with Natural Gas

Figure 3-8. Effect of sorbent additive (5% Fe_2O_3 by weight) on sulfur capture, sorbent injected with primary air (natural gas, SR_1 = 0.5, 0.3 MW_t).



Swirl Blocks (12)
Air Plenum
Jade Ram
KAOTAB 95
Block Mix.
KAOLITE 2800
1900°F Insul-Board

Figure 3-9. Cross-section of the VCC prototype combustor (0.9 MW_t).

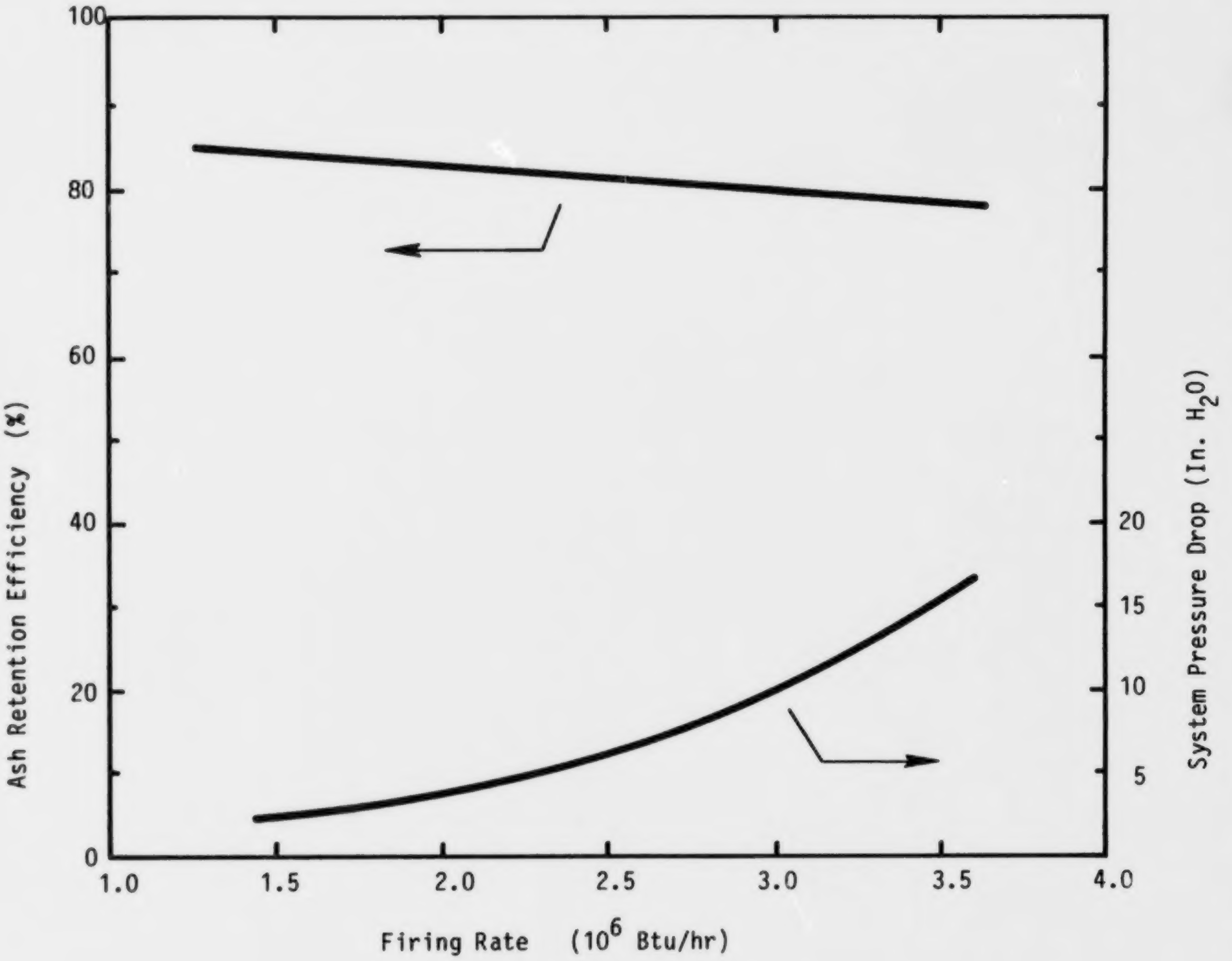


Figure 3-10. Recent ash retention efficiency measurements and system pressure drop versus firing rate (La Fond et al., 1986) in the VCC.

for staged operation and by over 85 percent when natural gas reburning was applied (see Figure 3-11).

A limited number of exploratory tests were performed to investigate SO_2 reduction by fuel-rich sorbent injection. Figure 3-12 shows the results of tests when Vicron 45-3 was injected into the VCC through auxiliary fuel injectors at varied stoichiometric ratio and Ca/S molar ratio. The results were discouraging, however, upon re-evaluation with the information gained from Phase II of this program these VCC results could be expected. The choice of operating stoichiometry, sorbent injection location and even sorbent type were not optimal.

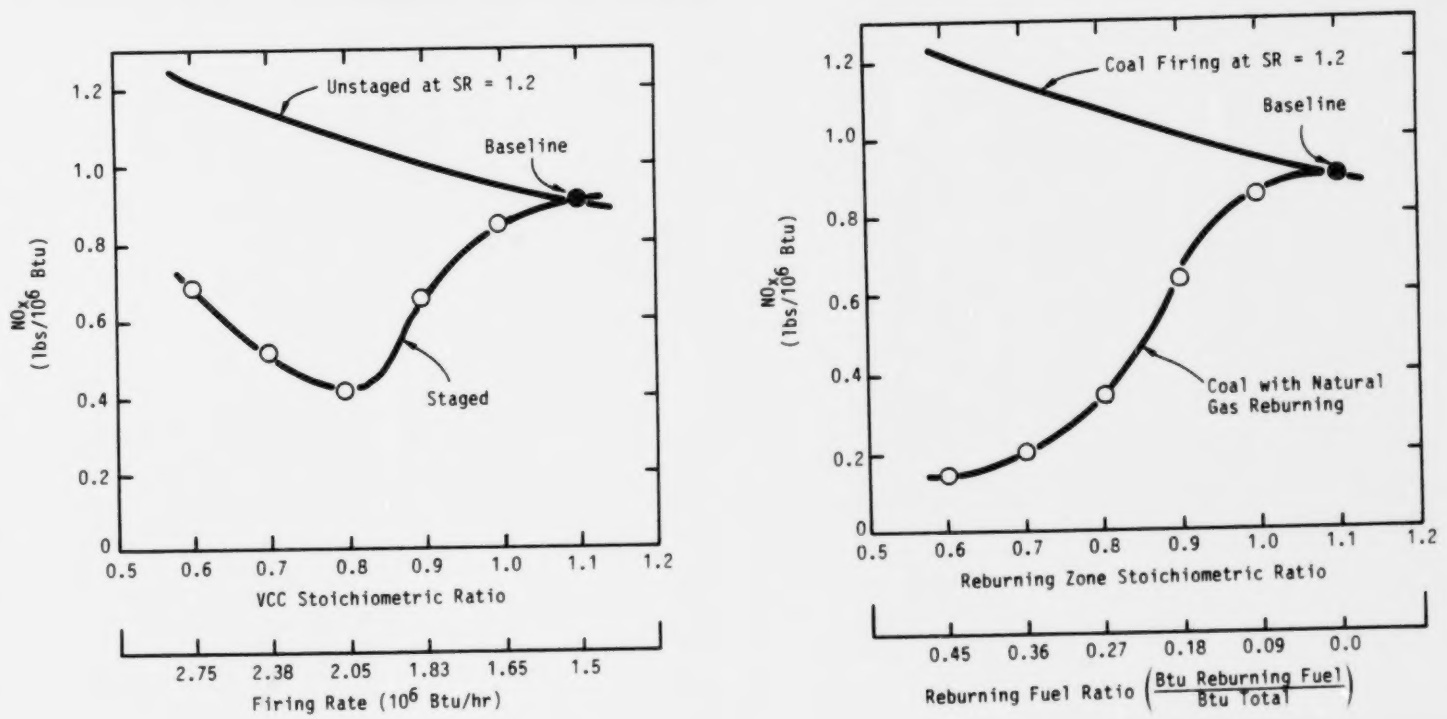
The VCC testing experience provided a great deal of insight into the operational difficulties that would be faced in trying to apply sulfur control technology to high firing density precombustor systems.

3.2 Review of Slag Related Industry and Research

Both the steel and glass industries have faced slag related problems over their histories. In the making of steel, slag additives have been used to help remove sulfur impurities from iron ore and steel melts. Additives have been used in the glass industry to lower slag melting times for production of glass. Review of this information was useful in preparing the program test plan and in utilizing the generated data.

The desulfurization process is a crucial step in the making of iron and steel. Sulfur is considered a contaminant that reduces the ductility and impact strength of iron and steel, and many years of research have been directed at its removal. In the production of iron, early desulfurization efforts concentrated on layering limestone into blast furnaces along with coke and iron ore (see Figure 3-13).

Wilson and McLean (1980) have pointed out that current practice concentrates on sulfur treating the pig iron after removal from the blast furnace. A schematic example of an iron desulfurization station is presented



(a) Combustion Staging

(b) Natural Gas Reburning

Figure 3-11. NO_x control by combustion staging and natural gas reburning in the VCC; Illinois coal, $SR_T = 1.2$ (La Fond et al., 1985).

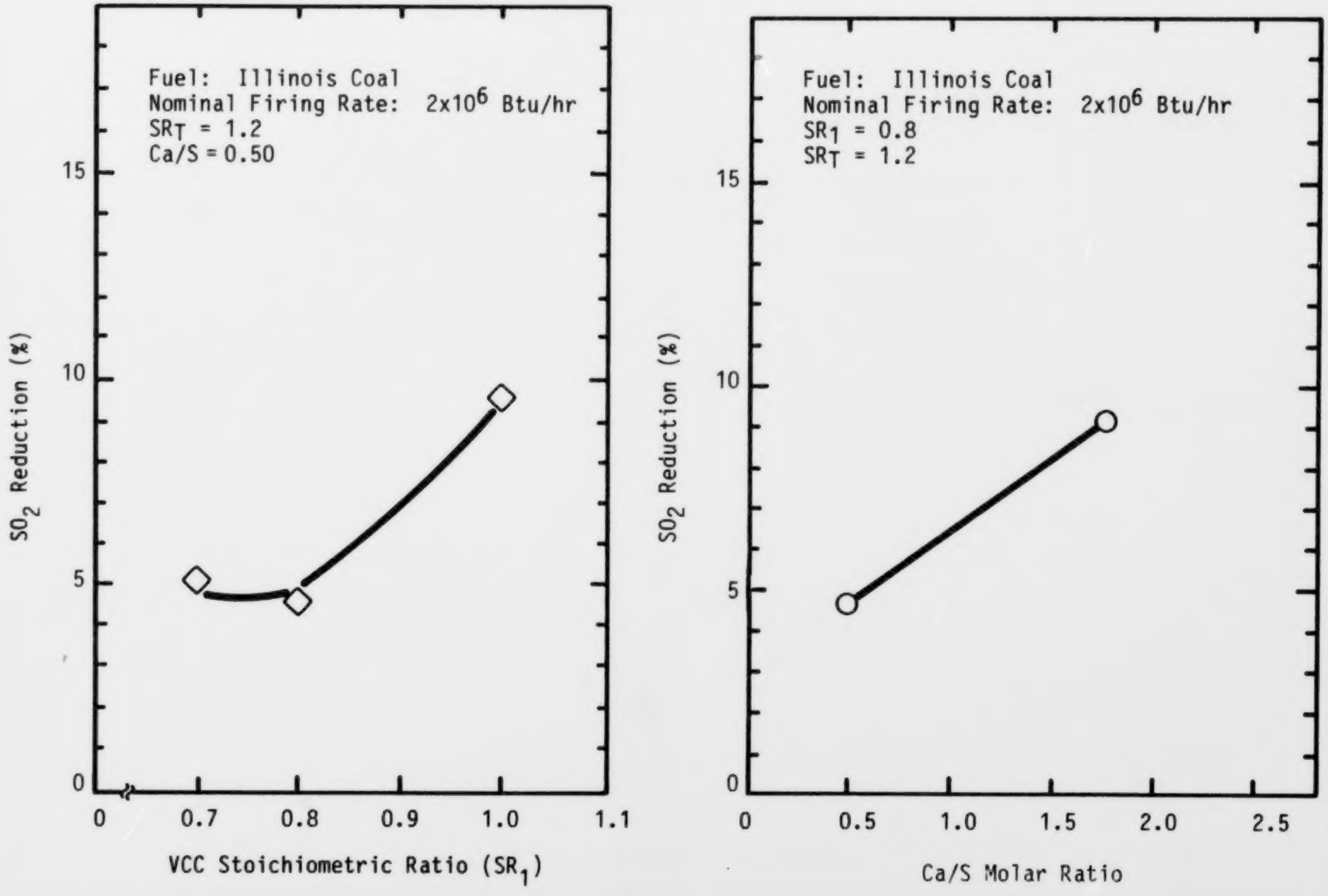


Figure 3-12. Effect of stoichiometry and Ca/S molar ratio on sulfur capture when injecting sorbent into the VCC under staging conditions (La Fond et al., 1986).

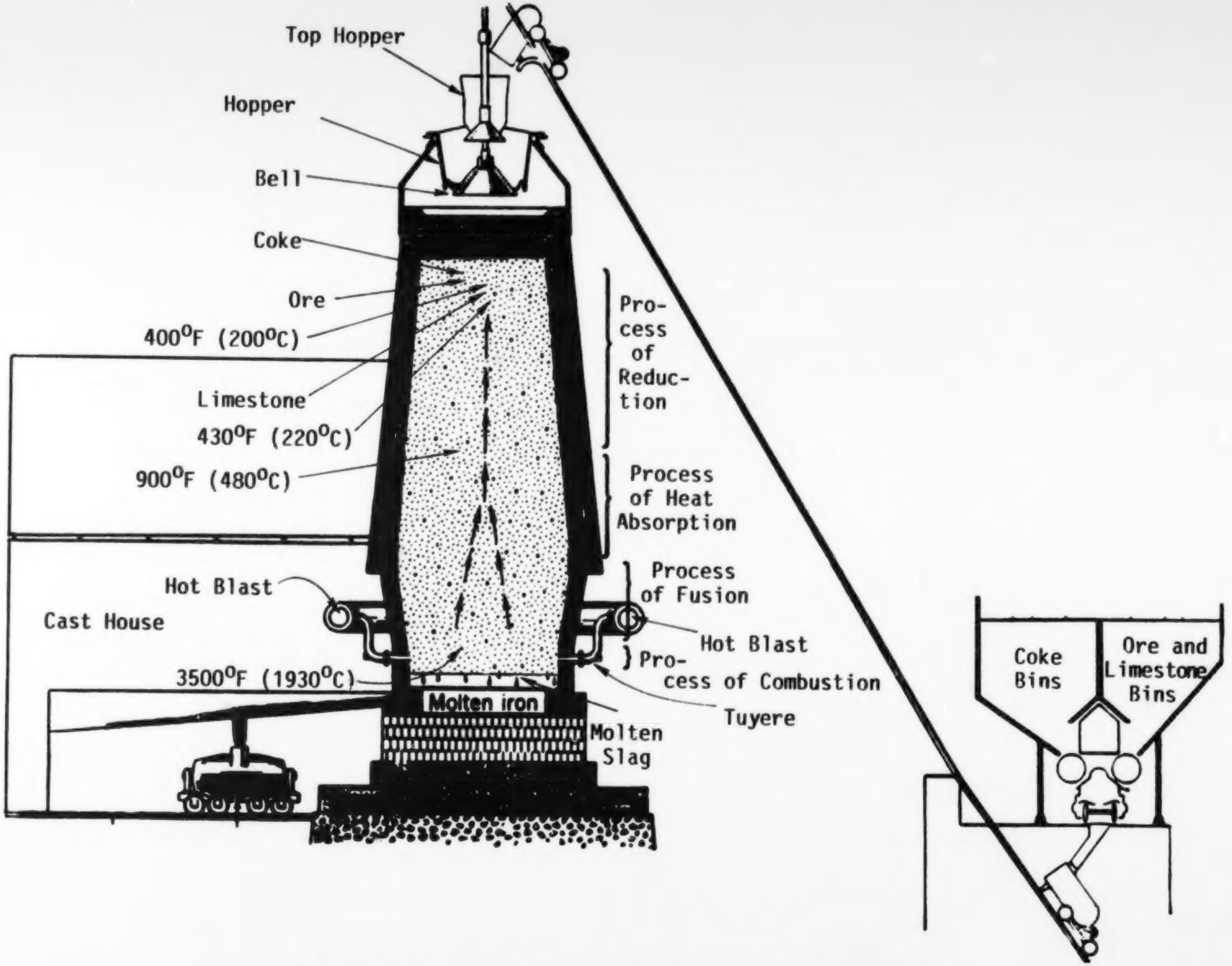

Top Hopper
Hopper
Bell
Coke
Ore
400°F (200°C)
Limestone
430°F (220°C)
900°F (480°C)
Process of Reduction
Process of Heat Absorption
Process of Fusion
Hot Blast
Cast House
Hot Blast
Process of Combustion
3500°F (1930°C)
Tuyere
Molten iron
Molten Slag
Coke Bins
Ore and Limestone Bins

Figure 3-13. Cross-sectional view of blast furnace.

in Figure 3-14. Additives for the removal of sulfur include: magnesium (pure powder, salt coated granules, mixtures with coke, mixtures with lime), rare earth metals (Cerium or Lanthanum), CaC_2, Na_2CO_3, CaO, and CaF_2. By processing the iron separate from the blast furnace, more economical operation of the blast furnace and improved desulfurization has been achieved. Several of these additives do not remove significant amounts of sulfur upon initial injection, but float to the top of the molten iron bath to form basic slags. Sulfur is then absorbed into the slag by ionic transfer between the two liquid materials.

The desulfurization process during the making of steel follows very similar patterns to the iron desulfurization process. Once the steel has been decarburized the same kinds of additives are used as were previously mentioned for iron making along with a few others: nickel-4.5 percent magnesium, CaSi, CaO + CaF_2 + Al mixtures. A critical step in the steel making desulfurization process is the reduction of the oxygen content to as low a level as possible. Si and Al additives help scavenge oxygen, making slag sulfide formation as CaS or MgS more favorable (Na_2CO_3 is seldom used today due to its corrosive attack on the furnace refractory linings). Similar desulfurization methods can be applied to open hearth furnaces, ladles, or induction ladle furnaces.

Desulfurization techniques were investigated more scientifically in the 1950's as the demand for higher quality steels increased. Of primary importance to these efforts was the establishment of sulfur capacity equilibrium for slag mixtures containing CaO (with some investigation of MgO based slags). Fincham and Richardson (1954), St. Pierre and Chipman (1956), and Carter and Macfarlane (1957) are examples of this early work. Their objective was to find compositions of $CaO-SiO_2-Al_2O_3$ based slags that had liquidus temperatures within the range required for steel making (1500 to 1650°C) and establish the sulfur capacity of those slags. Figure 3-15 presents some of the results of Fincham and Richardson (1954) establishing the solubility of sulfur in $CaO-SiO_2-Al_2O_3$ slag mixtures at 1650°C. These findings have been shown to hold true in practical steel desulfurization applications in studies by Sussman et al. (1982), as can be seen in

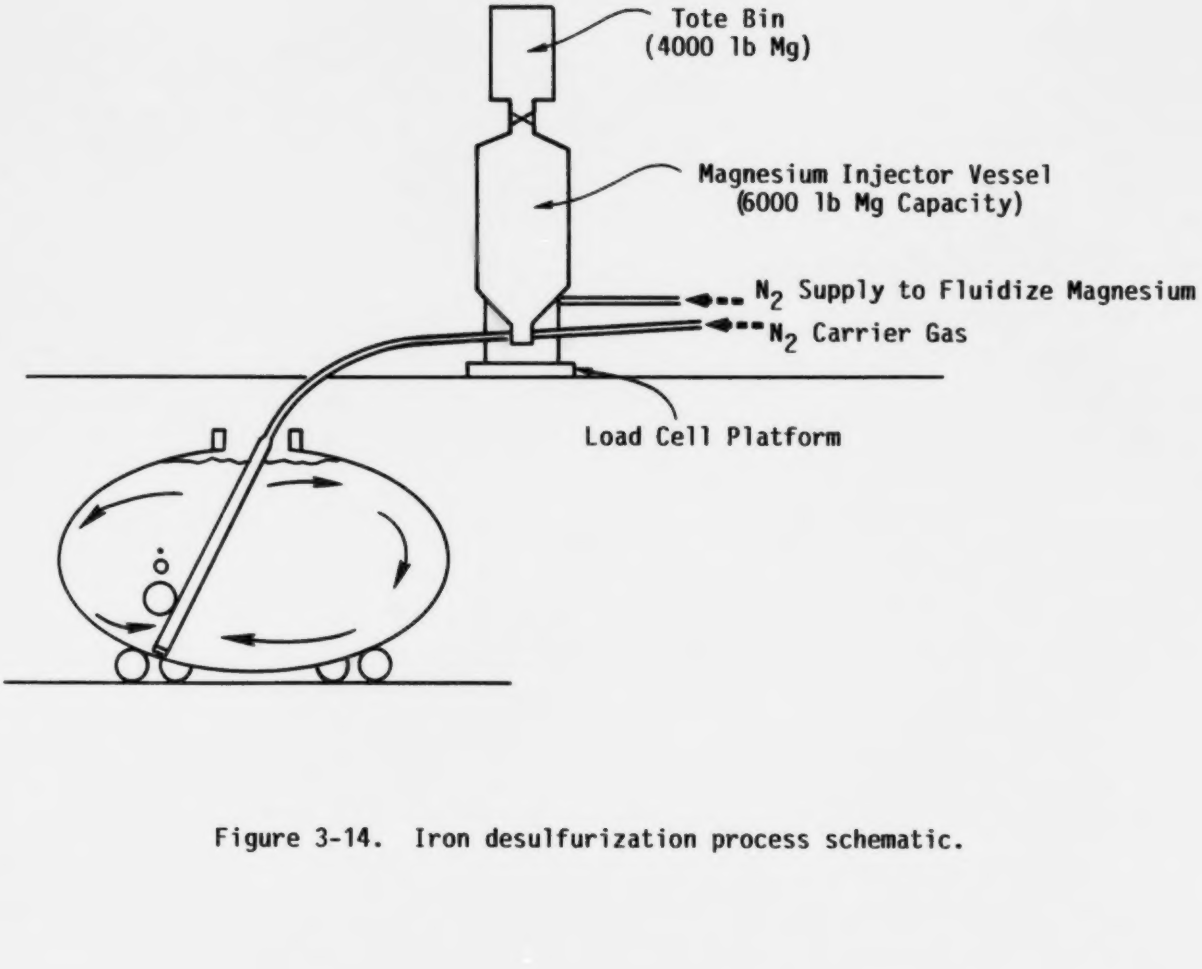
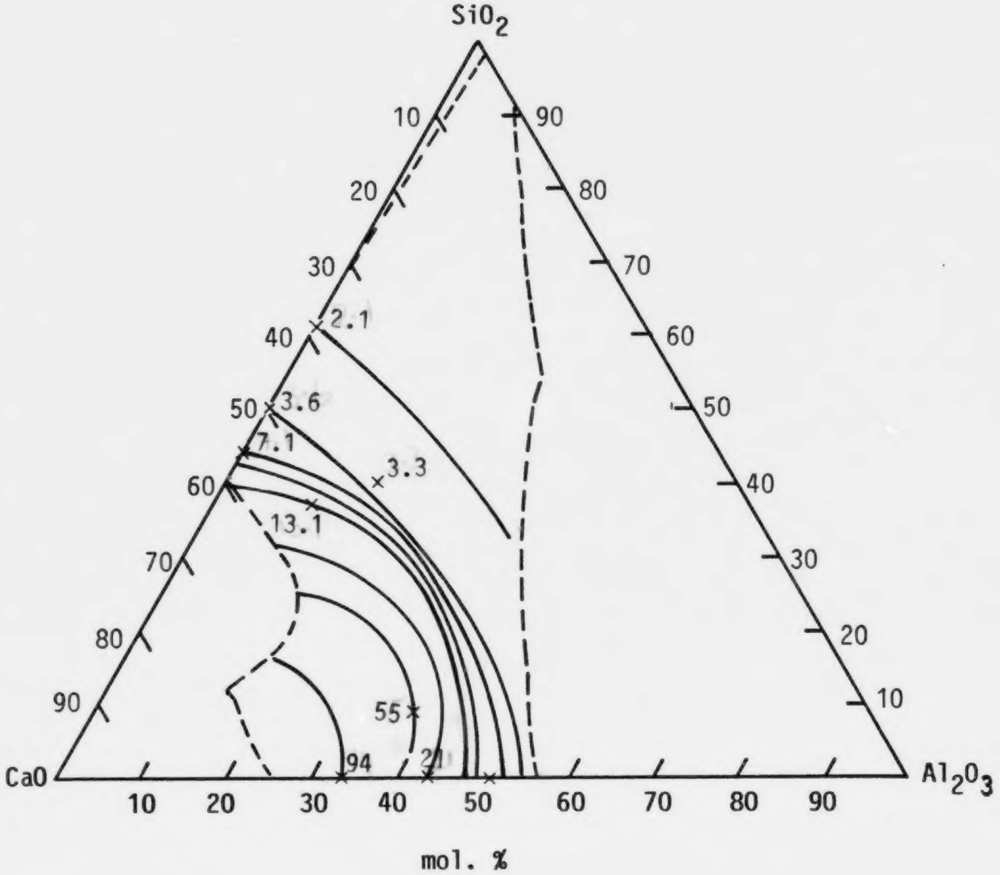

Tote Bin
(4000 lb Mg)
Magnesium Injector Vessel
(6000 lb Mg Capacity)
N_2 Supply to Fluidize Magnesium
N_2 Carrier Gas
Load Cell Platform

Figure 3-14. Iron desulfurization process schematic.



Values refer to $C_s \times 10^4$

where: C_s = (wt % S)

Pa = Partial pressure oxygen

P_{S_2} = Partial pressure gaseous sulfur species

Figure 3-15. Sulfur capacities, at 1650°C, in $CaO-SiO_2-Al_2O_3$ melts. Crosses are experimental points and broken lines are liquid composition limits at this temperature.

Figure 3-16 and Herrera et al. (1983). Unfortunately, ternary phase diagrams (from Levin et al., 1979) show that the liquidus temperature of the most reactive slags are high compared to conditions in coal combustion systems (see Figure 3-17).

Recently, DeYoung (1984) has completed an investigation of lower melting slag mixtures, including investigation of $FeO-Al_2O_3-SiO_2$ based slags. As Figures 3-18 and 3-19 indicate, slag mixtures with liquidus temperatures below 1200°C can be generated. Measurement of sulfur capacities in slags produced by mixtures of West Virginia coal ash and additives were made showing much greater equilibrium levels of sulfur in FeO based slags than CaO or Na_2O. Calculation of possible precombustor sulfur capture based on equilibrium gas phase concentrations were made for a range of sulfur capacities. The result of these equilibrium calculations along with a sulfur mass balance gave potential sulfur removal values as a function of the percentage of slag being injected into a precombustor system. These calculations showed that high sulfur capture in the slag was possible with $FeO-Al_2O_3-SiO_2$ based slags. However, no investigation of the kinetics of sulfur evolution and sulfur mass transfer into the slag was performed and extremely high levels of FeO were required.

Glass is defined by Doremus (1973) as an amorphous solid; it has no order in its structure, no crystallization. Glass is typically formed by rapidly cooling a material from the normal liquid state. The three main categories of glass are:

- Oxide
  - SiO_2
  - B_2O_3
  - GeO_2
  - P_2O_5
- Chalcogenide
  - Sulfur
  - Selenium
  - Tellurium
- Ionic
  - Halide
  - Nitrate
  - Sulfate
  - Carbonate

Of interest to this program is the role that B_2O_3 and P_2O_5 play in glass making and their influence on silicate formation when mixed with coal ash. In general, B_2O_3 and P_2O_5 have much lower viscosities than SiO_2 at the same

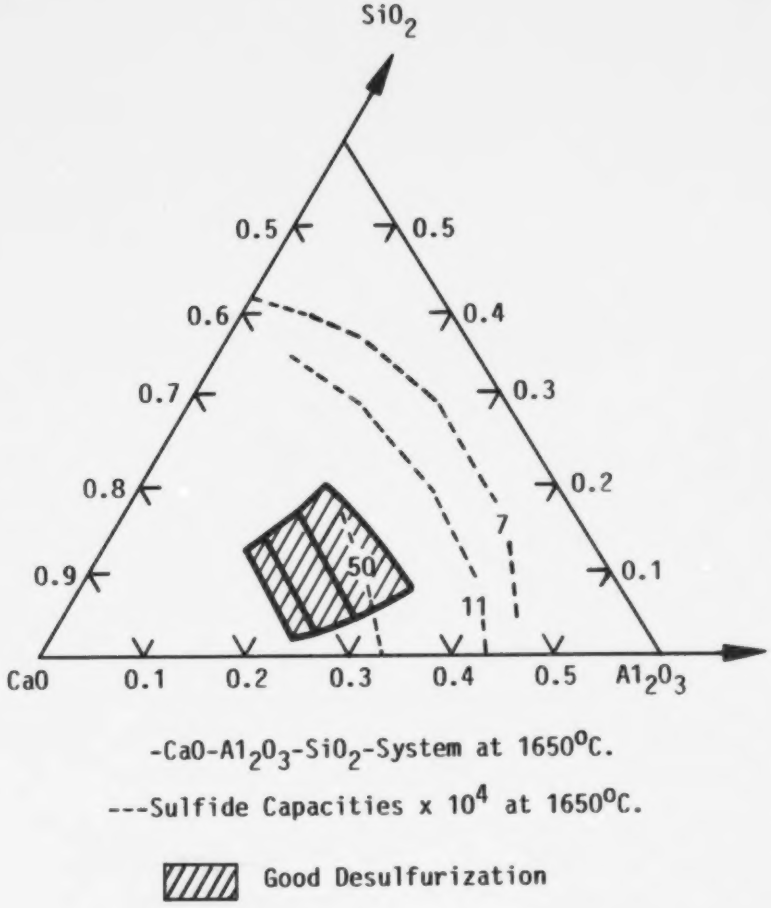


Figure 3-16. Desired slag compositions in the Armco top slag desulfurization process (Sussman et al., 1982).

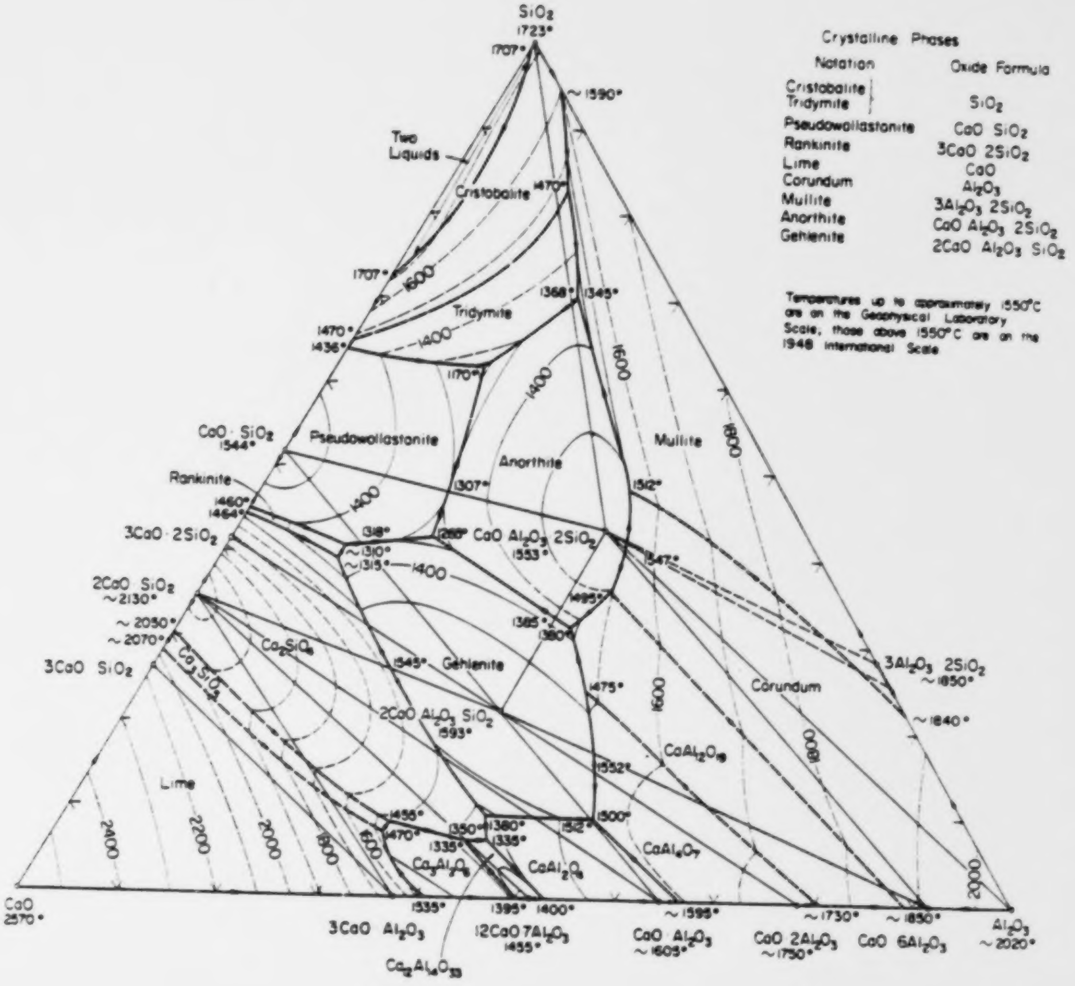

SiO2
1723°
1707°
~1590°
Two Liquids
Cristobalite
1470°
1707°
1600
Tridymite
1368°
1345°
1470°
1436°
1400
1170°
1400
1600
Mullite
1800
CaO·SiO2
1544°
Pseudowollastonite
Anorthite
Rankinite
1460°
1464°
1400
1307°
1512°
3CaO·2SiO2
1318°
1265° CaO Al2O3 2SiO2
1553°
~1310°
~1315°
1400
1547°
2CaO SiO2
~2130°
1495°
~2050°
~2070°
1385°
1380°
Ca2SiO4
3Al2O3 2SiO2
~1850°
3CaO SiO2
Ca3SiO5
1545° Gehlenite
1475°
Corundum
1600
2CaO Al2O3 SiO2
1593°
~1840°
1800
1552°
CaAl12O19
Lime
1455°
1500°
2400
2200
2000
1800
1600
1470°
1350°
1380°
1335°
1512°
1335°
Ca3Al2O6
CaAl2O4
CaAl4O7
2000
CaO
~2570°
1535°
1395°
1400°
~1595°
~1730°
~1850°
Al2O3
~2020°
3CaO Al2O3
12CaO 7Al2O3
1455°
CaO Al2O3
~1605°
CaO 2Al2O3
~1750°
CaO 6Al2O3
Ca12Al14O33
Crystalline Phases
Notation
Oxide Formula
Cristobalite
Tridymite
SiO2
Pseudowollastonite
CaO SiO2
Rankinite
3CaO 2SiO2
Lime
CaO
Corundum
Al2O3
Mullite
3Al2O3 2SiO2
Anorthite
CaO Al2O3 2SiO2
Gehlenite
2CaO Al2O3 SiO2
Temperatures up to approximately 1550°C are on the Geophysical Laboratory Scale; those above 1550°C are on the 1948 International Scale

Figure 3-17. Ternary diagram for $CaO-Al_2O_3-SiO_2$ melts; temperature in ^oC. Reprinted by permission of the American Ceramic Society (Levin, et al. 1964).

$FeO-Al_2O_3-SiO_2$

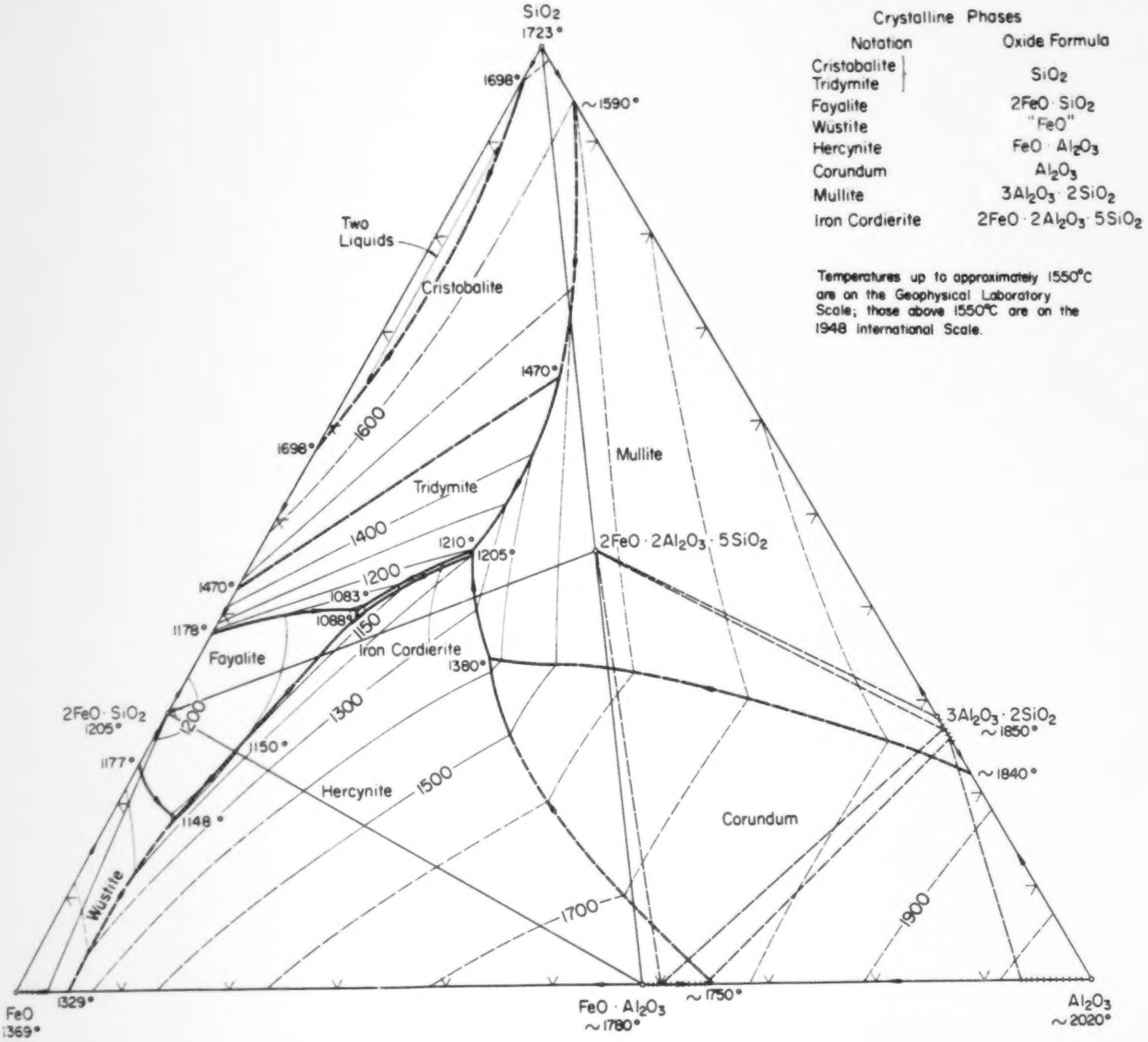

SiO2
1723°
1698°
~1590°
Crystalline Phases
Notation
Oxide Formula
Cristobalite
Tridymite
SiO2
Fayalite
2FeO · SiO2
Wustite
"FeO"
Hercynite
FeO · Al2O3
Corundum
Al2O3
Mullite
3Al2O3 · 2SiO2
Iron Cordierite
2FeO · 2Al2O3 · 5SiO2
Temperatures up to approximately 1550°C are on the Geophysical Laboratory Scale; those above 1550°C are on the 1948 International Scale.
Two Liquids
Cristobalite
1470°
1600
1698°
Mullite
Tridymite
1400
1210°
1205°
2FeO · 2Al2O3 · 5SiO2
1470°
1200
1083°
1178°
1088°
1150
Iron Cordierite
Fayalite
1380°
2FeO · SiO2
1205°
1300
1200
3Al2O3 · 2SiO2
~1850°
1177°
1150°
~1840°
Hercynite
1500
1148°
Corundum
Wustite
1700
1900
FeO
1369°
1329°
FeO · Al2O3
~1780°
~1750°
Al2O3
~2020°

Figure 3-18. Ternary diagram for $FeO-Al_2O_3-SiO_2$ melts; scales in weight percent and temperature in ^0C. Reprinted by permission of the American Ceramic Society (Levin et al. 1964).

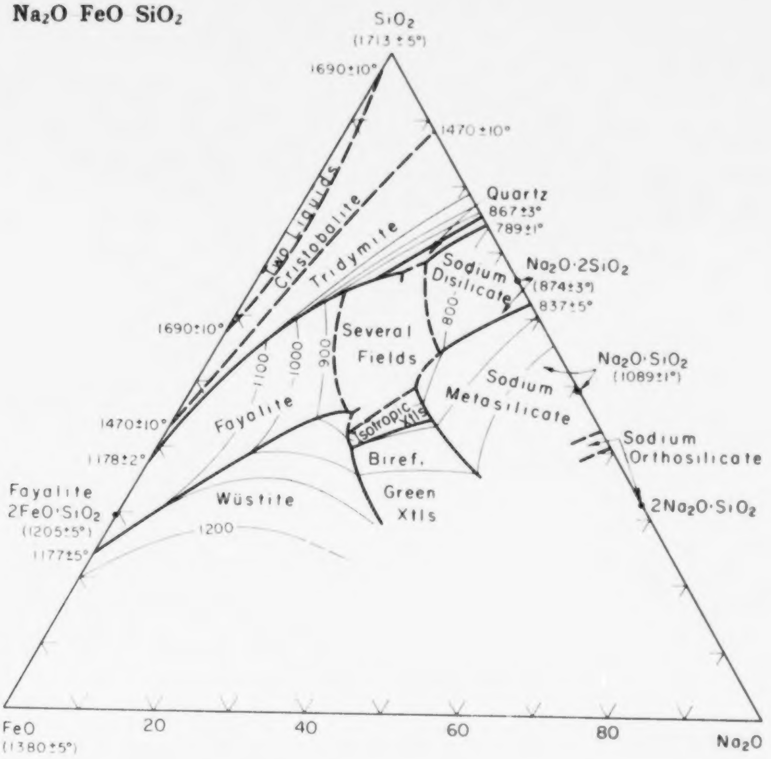

Na₂O FeO SiO₂
SiO₂
(1713 ± 5°)
1690±10°
1470±10°
Quartz
867±3°
789±1°
Two Liquids
Cristobalite
Tridymite
Sodium Disilicate
Na₂O·2SiO₂
(874±3°)
837±5°
1690±10°
Several Fields
800
900
1000
1100
Na₂O·SiO₂
(1089±1°)
Sodium Metasilicate
1470±10°
Fayalite
Isotropic Xtls
Sodium Orthosilicate
1178±2°
Biref.
Fayalite
2FeO·SiO₂
(1205±5°)
Wüstite
Green Xtls
2Na₂O·SiO₂
1200
1177±5°
FeO
(1380±5°)
20
40
60
80
Na₂O

Figure 3-19. Ternary diagram for FeO-Na_2O-SiO_2 melts; scales in weight percent and temperature in ^{o}C. Reprinted by permission of the American Ceramic Society (Levin, et al. 1969).

temperature. The addition of either of these oxides to silica lowers the mixture viscosity, with B_2O_3 being particularly effective.

The available literature suggests that the replacement of SiO_2 with B_2O_3 and P_2O_5 in slag mixtures can lower the fluid viscosity. According to Pye et al. (1972): "Small amounts of B_2O_3 or fluorides are also claimed to be helpful (in the glass melting process), probably by producing lower-melting phases initially or by decreasing viscosity over the entire temperature range of the melting process." Doyle (1979) has reported the time required for batches of Na_2O-CaO-B_2O_3-SiO_2 glass to melt at 1427°C (which is related to the batch melting temperature) as B_2O_3 is used to replace other components. As can be seen in Table 3-1, replacement of SiO_2 with B_2O_3 causes an initial lowering in the batch melting time.

The replacement of SiO_2 with B_2O_3 and P_2O_5 can also reduce the formation of silicates. It is the formation of silicates that appears to be the most damaging factor in reducing the sulfur capacity of a slag mixture. However, if B_2O_3 or P_2O_5 is used as an additive, the addition of more glass making material may cause additional reductions in sulfur capacity due to borate or phosphate formation. Data by Abraham and Richardson (1960) shows that the addition of 7 percent P_2O_5 to both CaO-Al_2O_3 and CaO-SiO_2 mixtures caused a lowering of the sulfur capacity and that mixtures of CaO-P_2O_5 had lower sulfur capacities than either the CaO-Al_2O_3 or CaO-SiO_2 systems of the same CaO fraction (see Figure 3-20).

The only available data on sulfur capacity when adding B_2O_3 was performed by DeYoung (1984). DeYoung found that by replacing 5 percent of the SiO_2 with B_2O_3 in a FeO-Al_2O_3-SiO_2 melt the sulfur capacity was unchanged. A similar experiment using P_2O_5 resulted in a reduction in the sulfur capacity of approximately 20 percent.

From the available literature it appeared that there may be some benefits to the use of B_2O_3 and P_2O_5 as slag additives in a coal-fired precombustor system.

TABLE 3-1. EFFECT OF B_2O_3 SUBSTITUTIONS ON MELTING TIME FOR THE Na_2O-CaO-B_2O_3-SiO_2 SYSTEM (Information from Doyle, 1979).

	Composition, %				Time (min) to obtain batch-free glass at 1,427°C
	B_2O_3	Na_2O	CaO	SiO_2	
B_2O_3 for Na_2O	0	14	12	74	13
	0.25	13.75	12	74	11
	0.50	13.50	12	74	12
	1	13	12	74	15
	3	11	12	74	36
	5	9	12	74	83
B_2O_3 for CaO	0	14	12	74	13
	0.5	14	11.5	74	11.5
	1	14	11	74	12.5
	3	14	9	74	20
	5	14	7	74	31
B_2O_3 for SiO_2	0	14	12	74	13
	0.5	14	12	73.5	10.5
	1	14	12	73	10.5
	3	14	12	71	10.5
	5	14	12	69	10.5
B_2O_3 for Na_2O + SiO_2	0	14	12	74	13
	0.5	13.75	12	73.75	12
	1	13.50	12	73.50	14
	3	12.50	12	73.50	24
	5	11.50	12	71.5	43

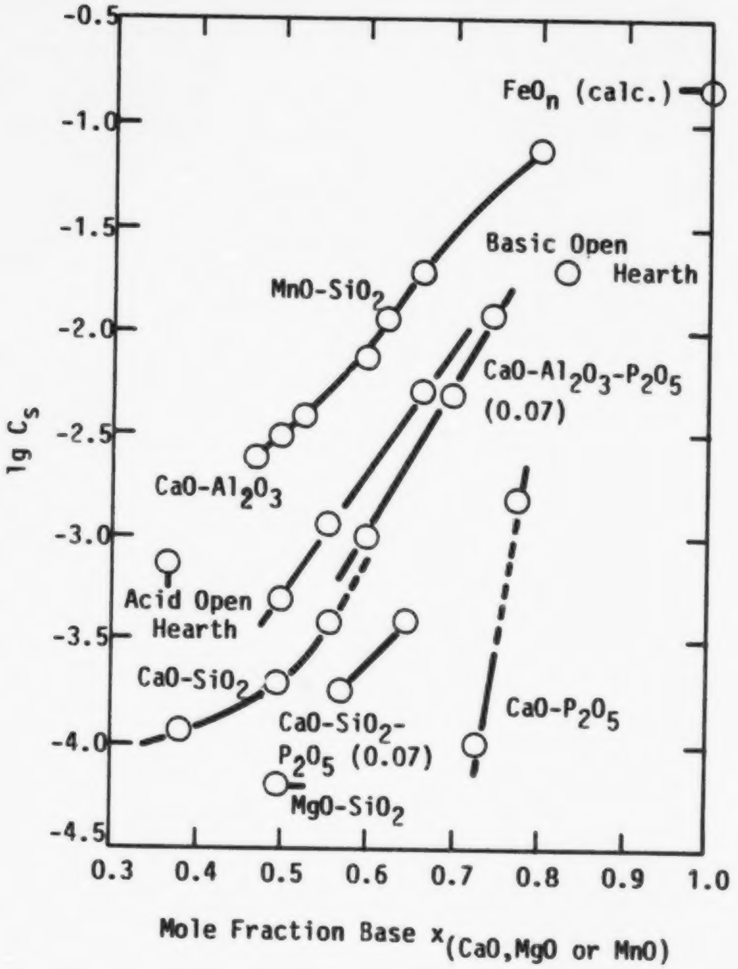


Figure 3-20. Sulfur capacities C_s, in various slag systems at 1650°C (information from Abraham and Richardson, 1960).

The review of slag related literature did not provide examples of slag-sulfur systems that were exactly comparable to the environment expected within coal-fired precombustor systems. However, the measurement and computational procedures developed by the metallurgical industry to predict expected equilibrium sulfur capture levels in slags proved to be very valuable in the development of precombustor slag testing performed in this program. Also, the glass industries use of B_2O_3 and P_2O_5 gave insight into possible slag fluxing agents for use in precombustor systems.

3.3 Calcium Sulfidation

The kinetics of calcium sulfide formation due to reactions between calcined limestone particles (CaO) and H_2S and COS has been studied extensively at the laboratory scale by Borgwardt et al. (1984a). Borgwardt also provides a good review and critique of previous kinetic studies of CaS formation. This work was performed in an isothermal differential reactor fabricated of quartz glass. The experiments were performed at low temperature with pure gases and CaO of known specific surface area.

By extrapolation of Borgwardt's kinetic data it was predicted that CaO with a specific surface area of 40 m^2/g reacting with 5000 ppm H_2S would have 40 percent conversion to CaS in only 0.04 seconds at 1250°C (2282°F). The addition of hydrogen (H_2) or chlorine (as $CaCl_2$) reduced conversion by 10 to 20 percent (relative) which for a Ca/S molar ratio of 2 would still result in about 65 to 70 percent sulfur capture under these conditions; that is, assuming capture increases linearly with Ca/S ratio.

It would be expected that sorbents that are most reactive under fuel-lean sulfation conditions are most reactive under fuel-rich sulfidation since reactivity has been shown by Borgwardt et al. (1984a and 1984b) to be dominated by specific surface area for both the sulfation and sulfidation reactions. A comparison of SO_2 capture by sulfate formation for two calcium carbonates and two calcium hydroxides is presented in Figure 3-21 (from Overmoe et al., 1986). Thus, the use of the most reactive sorbent, Linwood calcium hydroxide, would provide the clearest measure of sulfidation and

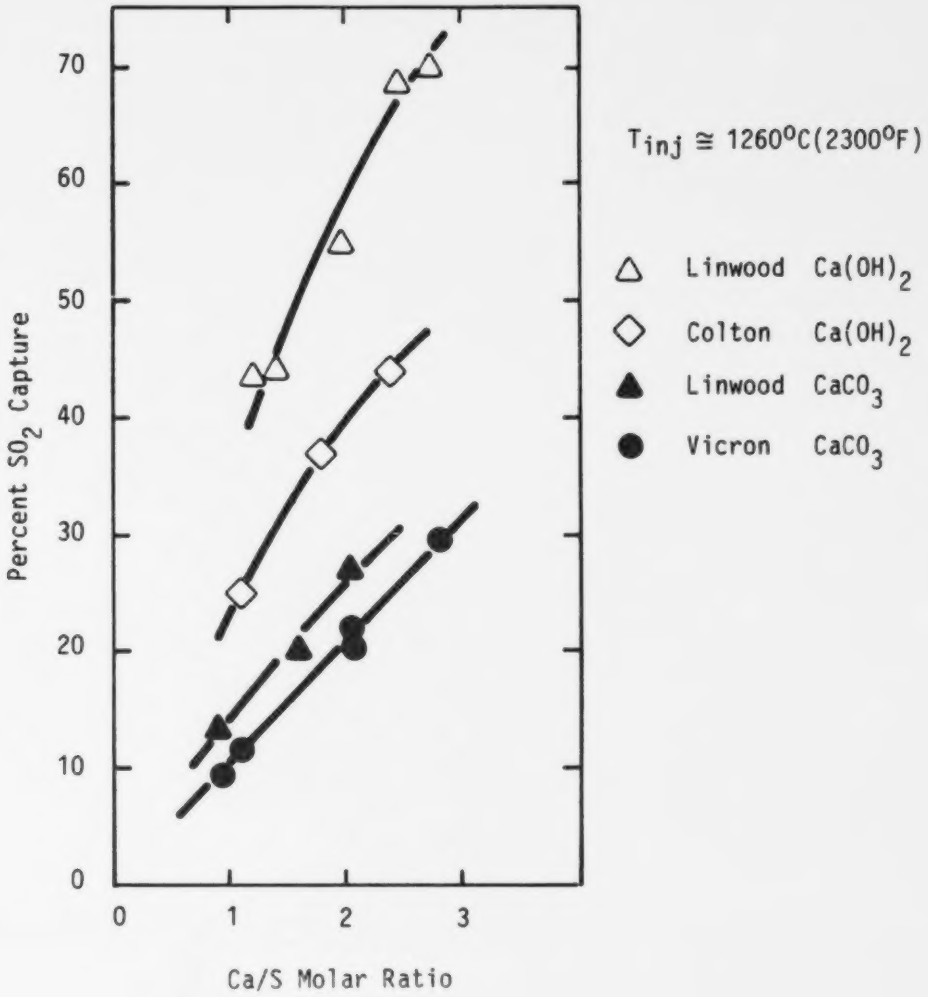


Figure 3-21. Comparison of sulfur capture capability for four different sorbent materials under fuel-lean conditions (Overmoe et al., 1986).

would most easily identify optimal operating conditions during parametric testing.

There was evidence during the Phase I testing that the sulfur captured in the fuel-rich precombustor was all in the form of CaS. Also, the data suggested that a majority of the CaS oxidized to CaO and SO_2 in the fuel-lean burnout region of the precombustor system. This problem of fuel-lean sulfur generation was investigated briefly by Cole et al. (1985a) in an isothermal drop-tube reactor. As Figure 3-22 shows, at typical combustion temperatures under fuel-lean conditions, CaS decomposes within 150 ms. Note, however, that the degree of regeneration reaches an asymptotic value of 80 percent. This may explain some of the Phase I results. The improvement in SO_2 capture when sulfur was introduced with the sorbent into the fuel-rich precombustor compared to when the sulfur was added with the secondary air can be accounted for by the carryover of CaS that did not decompose by exposure to the secondary flame.

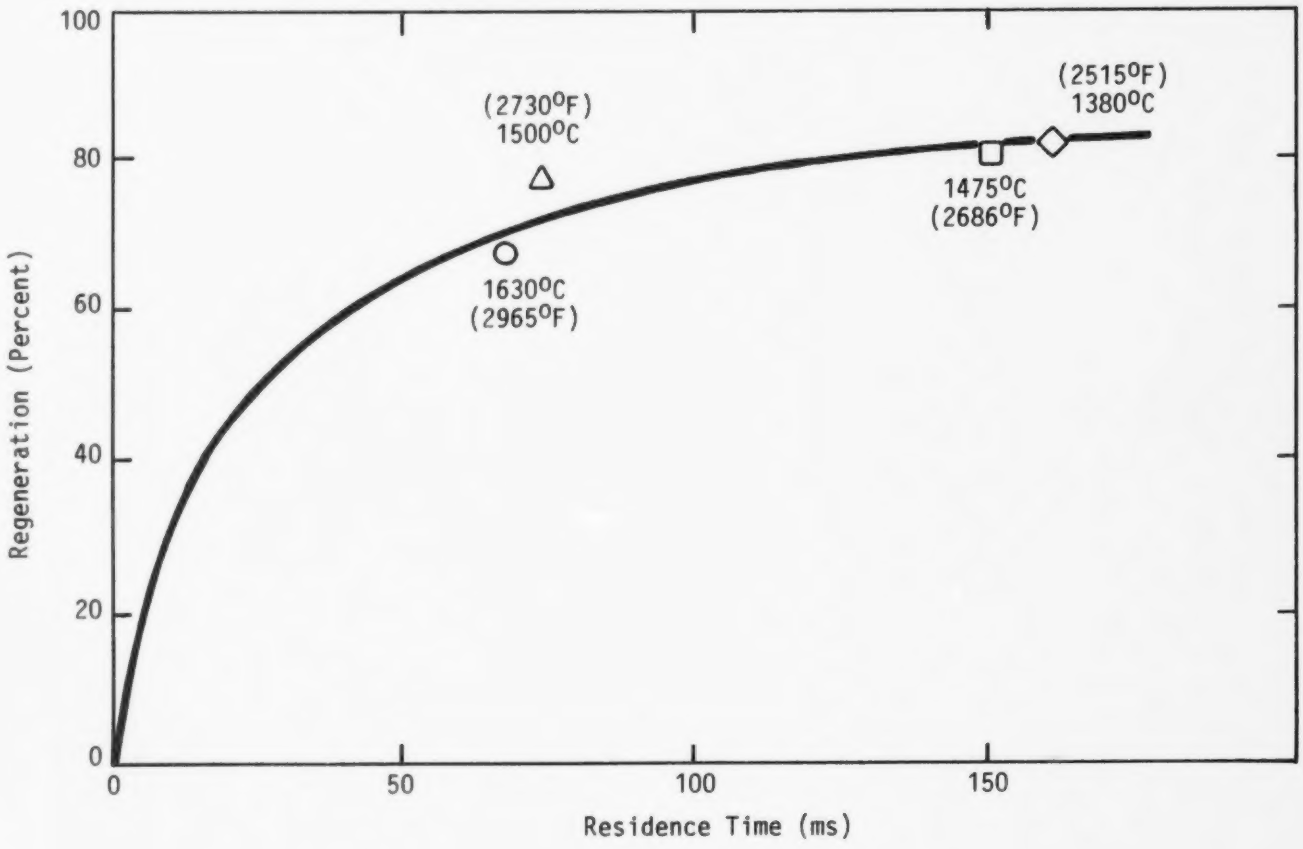


Figure 3-22. Regeneration of CaS with time for fuel-lean methane flames (Cole et al., 1985a).

4.0 OBJECTIVES AND APPROACH

The objective of this program was to reach a better understanding of fuel-rich sulfur control mechanisms and their relationship to other key precombustor operational processes such as carbon burnout, particulate emissions control, NO_x emissions control, and continuous slag drainage. This was done by carrying out a detailed investigation of several key process elements in the fuel-rich capture process. These elements included: 1) the formation of stable sulfides in the entrained flow region of a precombustor using calcium-based sorbents, 2) the evolution of sulfur (and other species) from coal in an entrained flow process, and 3) the solubility and stability of sulfur in molten slag layers.

Figure 4-1 presents a flow chart of the overall program approach. Phase I was a concept screening phase which resulted in a demonstration of the potential of simultaneous control of NO_x, SO_x and particulate emissions from a precombustor at the pilot scale and identified several key issues to be addressed in the Phase II testing.

Three facilities were utilized in Phase II of the program. The Isothermal Reactor facility (ITR) was used to investigate the formation of sulfides from the injection of calcium-based sorbents into the exhaust of gaseous fuel flames doped with H_2S. The ITR provided a well controlled reaction atmosphere (in terms of temperature and residence time) for the investigation of particular reactions and identification of key operating conditions.

The evolution of sulfur from coal and its subsequent reaction with sorbent was investigated in the Control Temperature Tower facility (CTT). The CTT was larger and less fragile than the ITR so as to accommodate coal firing. Gas phase sampling and analysis by gas chromatography allowed identification of sulfur speciation. Solids sampling and analysis identified the evolution of the major elements and provided a cross-check of gas phase sulfidation results.

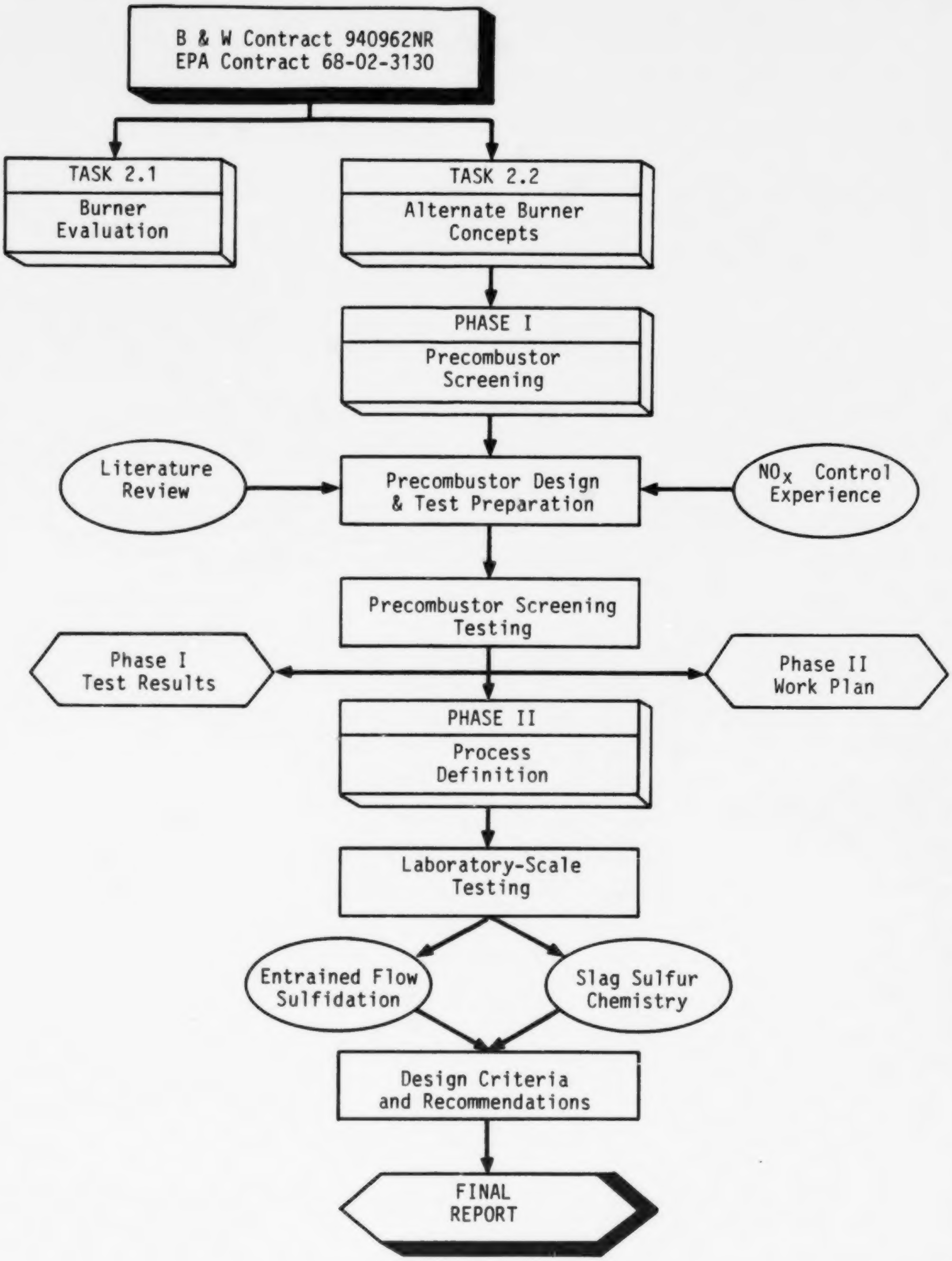

B & W Contract 940962NR
EPA Contract 68-02-3130
TASK 2.1
Burner Evaluation
TASK 2.2
Alternate Burner Concepts
PHASE I
Precombustor Screening
Literature Review
Precombustor Design & Test Preparation
NO$_x$ Control Experience
Precombustor Screening Testing
Phase I Test Results
Phase II Work Plan
PHASE II
Process Definition
Laboratory-Scale Testing
Entrained Flow Sulfidation
Slag Sulfur Chemistry
Design Criteria and Recommendations
FINAL REPORT

Figure 4-1. Program approach flow-chart.

The third facility utilized was constructed specifically for this work and is referred to as the High Temperature Oven facility (HTO). The system consisted of a high temperature tube furnace coupled to a gas blending system. Tests were performed to determine the equilibrium level of sulfur obtained in various slag-CaO mixtures, the rate at which CaS decomposes in molten slags, and the influence of fluxing additives on the capacity of the slags to hold sulfur and the fluidity of slags.

5.0 EXPERIMENTAL SYSTEMS

Three experimental facilities were used in this program: a laboratory-scale Isothermal Reactor (ITR); a bench-scale Control Temperature Tower (CTT); and a laboratory-scale High Temperature Oven (HTO).

5.1 Isothermal Reactor (ITR)

A cross-sectional view of the ITR is shown in Figure 5-1. The reaction chamber was centered in a 21 kW (72,000 Btu/hr) Lindberg furnace with maximum operating temperature of 1500°C (2700°F). The heated zone was 0.9 m (35 inches) long and could hold a 10 cm (4 inches) diameter reaction tube. Three independently controlled heating zones, separated by baffles, ensured that a flat temperature profile was maintained over the heated length.

The ITR was downfired by a precombustor assembly coupled with a sliding burner, as shown in Figure 5-2. There are two main features to this assembly: a sliding burner and a venturi. The sliding burner was a premixed, water cooled, flat-flame burner in a square stainless steel chimney. Due to heat losses through the chimney, variance of the burner position allowed downstream temperature control independent of the gas velocity and burner stoichiometry. The venturi, located immediately downstream of the sorbent injector/flow straightener, created turbulence which enhanced sorbent dispersion in the flame gases. The gradually divergent section after the venturi throat prevented backmixing and promoted a flat velocity profile.

The sorbent injector utilized swirl ports near the injector outlet to produce additional dispersion of the sorbent as it mixed with the reaction gases. Solid or gas sampling probes were inserted axially at the exhaust end of the reactor. Different reaction residence times were achieved by varying the elevation of a probe tip in the reactor.

Table 5-1 presents temperature data taken radially along the ITR length to demonstrate the level of temperature uniformity throughout the reactor.

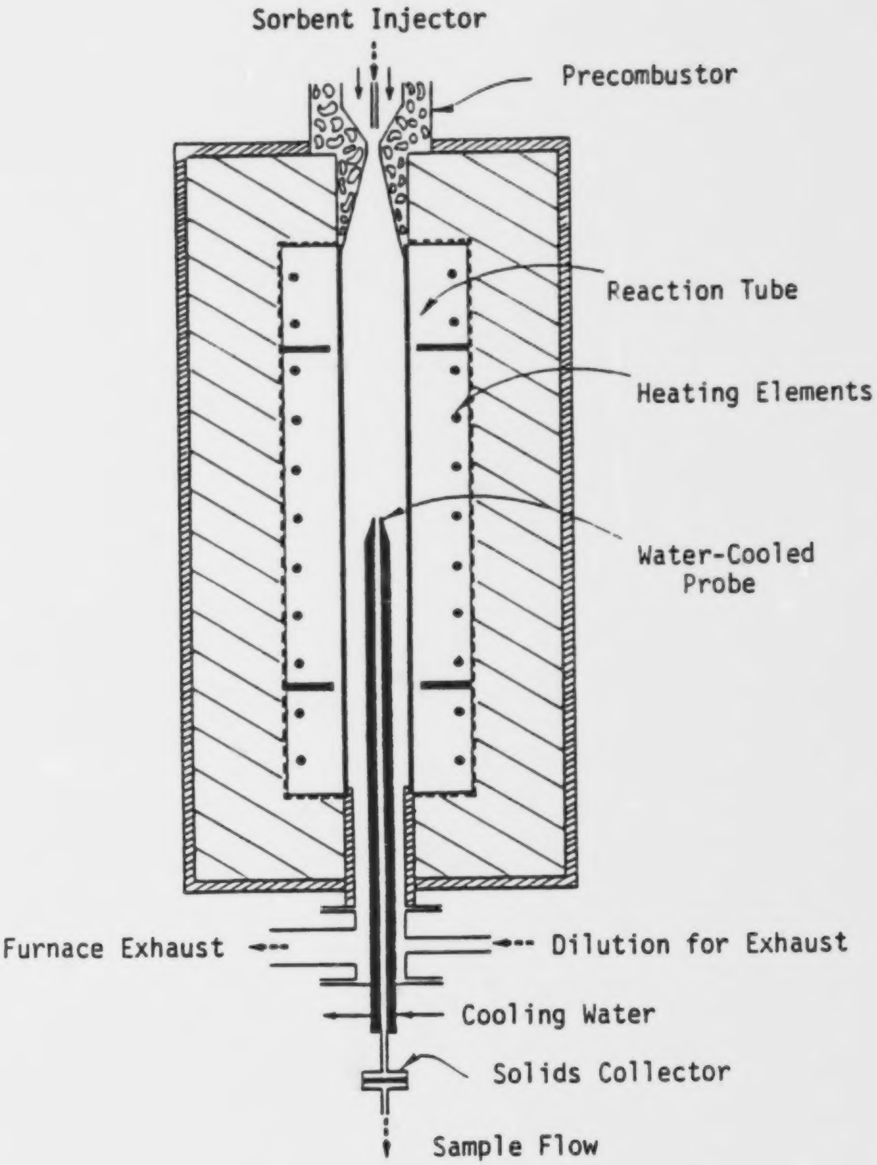

Sorbent Injector
Precombustor
Reaction Tube
Heating Elements
Water-Cooled Probe
Furnace Exhaust
Dilution for Exhaust
Cooling Water
Solids Collector
Sample Flow

Figure 5-1. Schematic of the isothermal reactor (ITR).

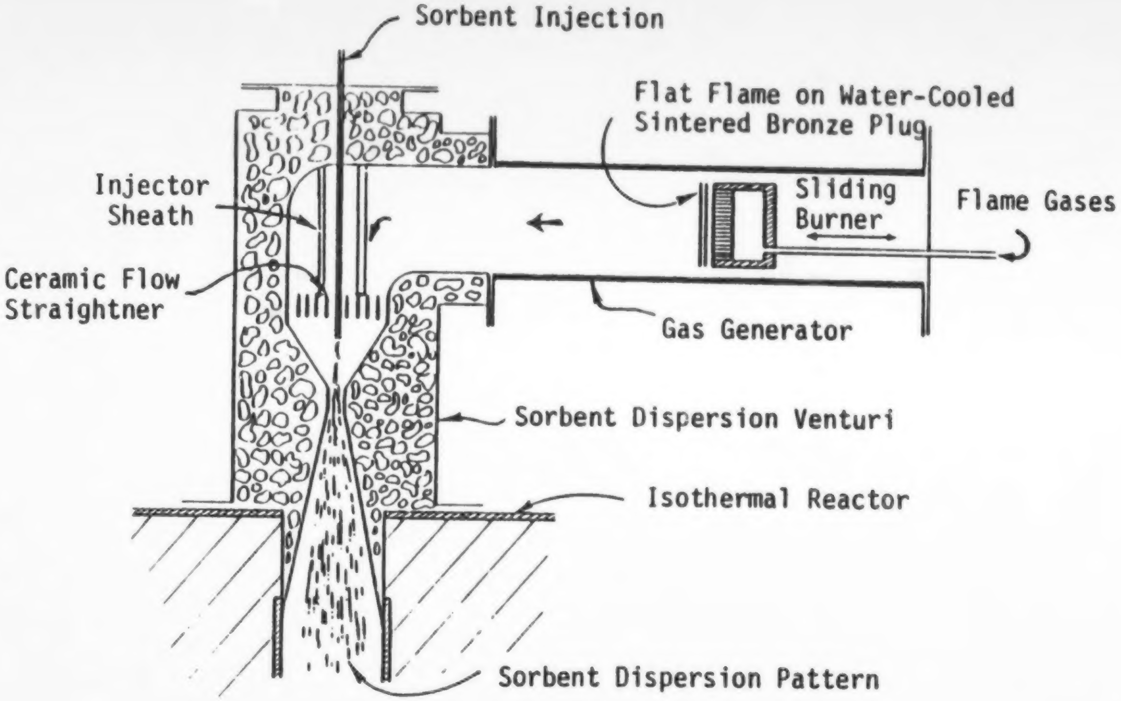

Sorbent Injection
Flat Flame on Water-Cooled Sintered Bronze Plug
Injector Sheath
Sliding Burner
Flame Gases
Ceramic Flow Straightner
Gas Generator
Sorbent Dispersion Venturi
Isothermal Reactor
Sorbent Dispersion Pattern

Figure 5-2. Schematic detail of the precombustor/sliding burner assembly.

TABLE 5-1. TEMPERATURE VARIATION IN THE ITR AT A NOMINAL 900°C ISOTHERMAL CONDITION

Distance from Burner, cm	Temperature, °C				
	Axis	N	S	E	W
107	897	895	895	899	895
94	909 905	910 906	911 904	910 904	910 900
81	904 903	907 905	909 906	906 902	910 905
69	903 904	902 906	908 911	904 910	906 913
56	903 909	902 908	912 916	901 913	907 912
43	903 902	902 904	910 906	909 903	906 909
30	900	898	896	902	898

5.2 Control Temperature Tower (CTT)

An overall diagram of the CTT furnace is presented in Figure 5-3. The reactor entry (top section) includes a 45.7 cm (18 inches) long quarl that diverges from 5.1 cm (2 inches) to 20.3 cm (8 inches). The long quarl provided flame stabilization as well as established a one-dimensional flow pattern. Numerous ports located along the axis of the reactor enabled supplementary equipment; i.e., zone separation chokes, fuel and air injectors, and cooling coils, to be placed in the reactor.

The CTT had the capability of manipulating the time/temperature profile by firing two sets of back-fired heating sections (second and fourth sections from the top). The back-fired sections employed natural gas burners which fired in the direction opposite to the main combustion gas. The back-fired effluent passed through channels in the refractory walls surrounding the main combustion zone (see the radial cross-sectional view in Figure 5-3). Backfiring in this manner minimized the temperature decay of the combustion products in the main combustion zone.

Each section of the CTT was fabricated from a 91.4 cm (36 inches) diameter steel shell (0.32 cm (1/8 inch) thick), two layers of castable insulation and two layers of castable refractory. The multi-layer design of the CTT is illustrated in Figure 5-4.

To best simulate the gas phase thermal environment of a precombustor system, the CTT was operated with both backfired sections on to minimize heat loss and maintain as close to an isothermal reaction zone as possible. The fuel-rich and secondary burnout stages were separated by a 10.2 cm (4 inch) ID choke to prevent backmixing of burnout air into the fuel-rich reaction zone. The choke was located 155 cm (61 inches) from the burner entry.

The cross-sectional layout of the premixed burner used on the CTT is shown in Figure 5-5. The primary air and fuel (natural gas or coal) were injected radially outward through six 0.32 cm (13/16 inch) holes into a mixing chamber. The preheated secondary air is injected radially inward into

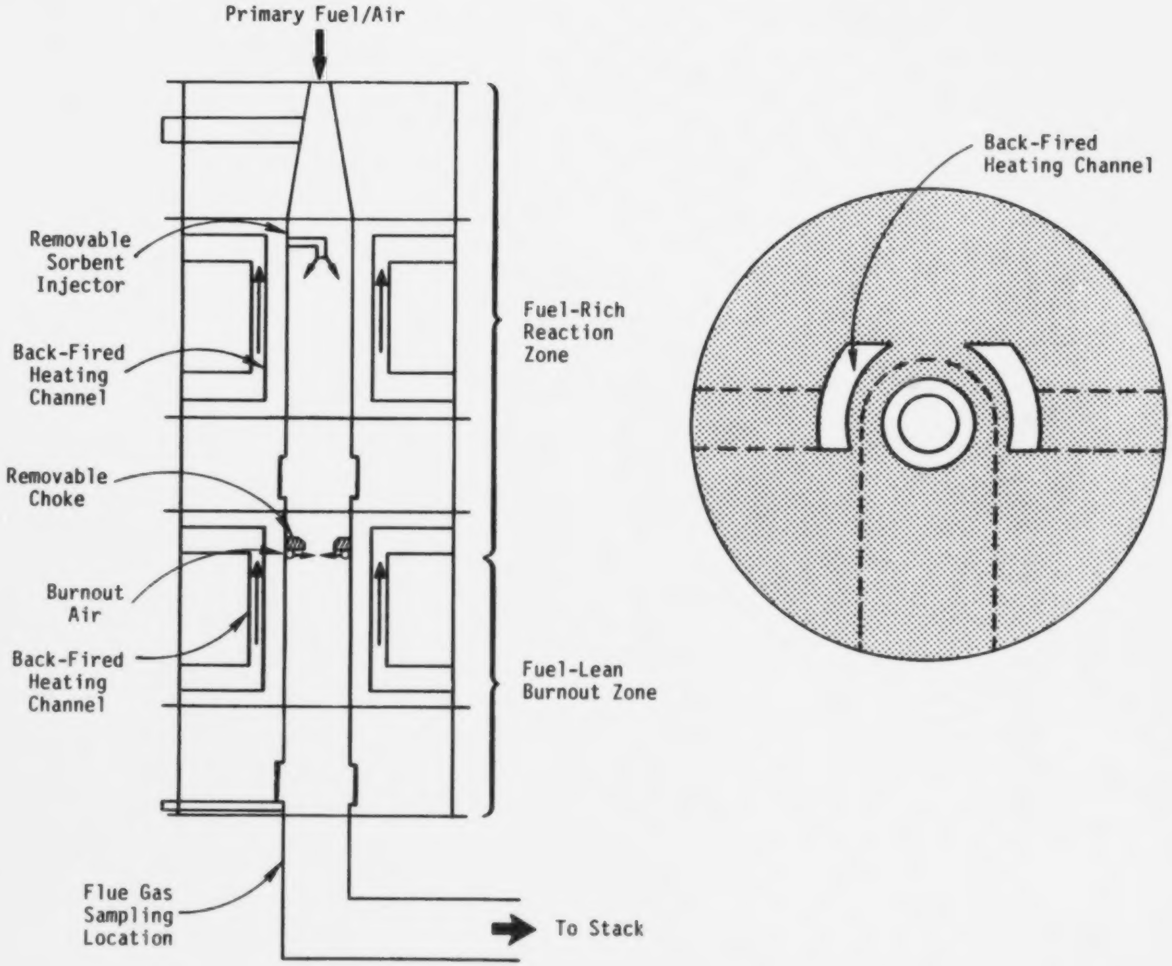

Primary Fuel/Air
Removable Sorbent Injector
Back-Fired Heating Channel
Removable Choke
Burnout Air
Back-Fired Heating Channel
Flue Gas Sampling Location
Fuel-Rich Reaction Zone
Fuel-Lean Burnout Zone
To Stack
Back-Fired Heating Channel

Figure 5-3. Cross-sectional views of the CTT configured with a fuel-rich zone.

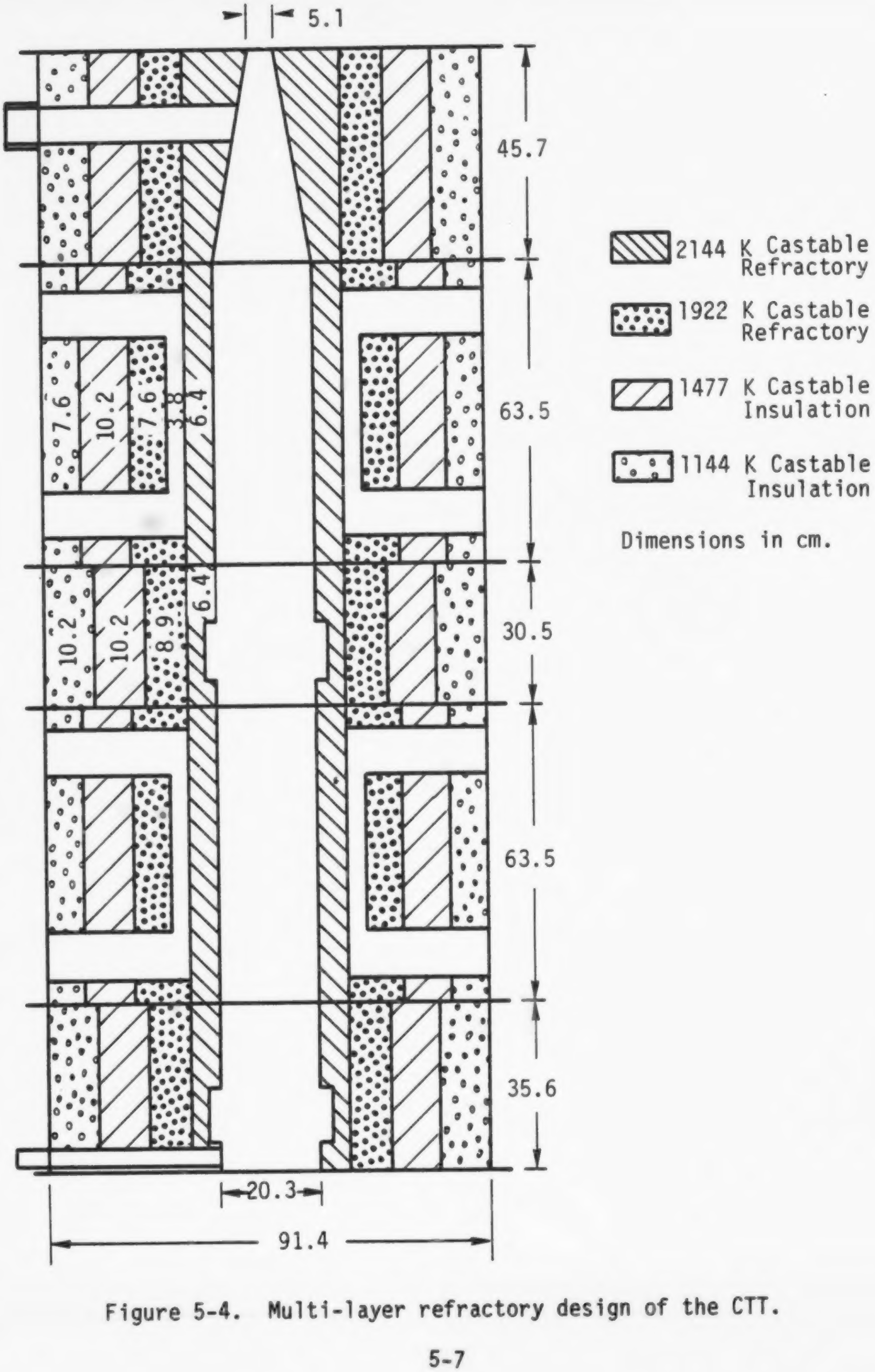

5.1
45.7
63.5
30.5
63.5
35.6
7.6
10.2
7.6
3.8
6.4
10.2
10.2
8.9
6.4
20.3
91.4
2144 K Castable Refractory
1922 K Castable Refractory
1477 K Castable Insulation
1144 K Castable Insulation
Dimensions in cm.

Figure 5-4. Multi-layer refractory design of the CTT.

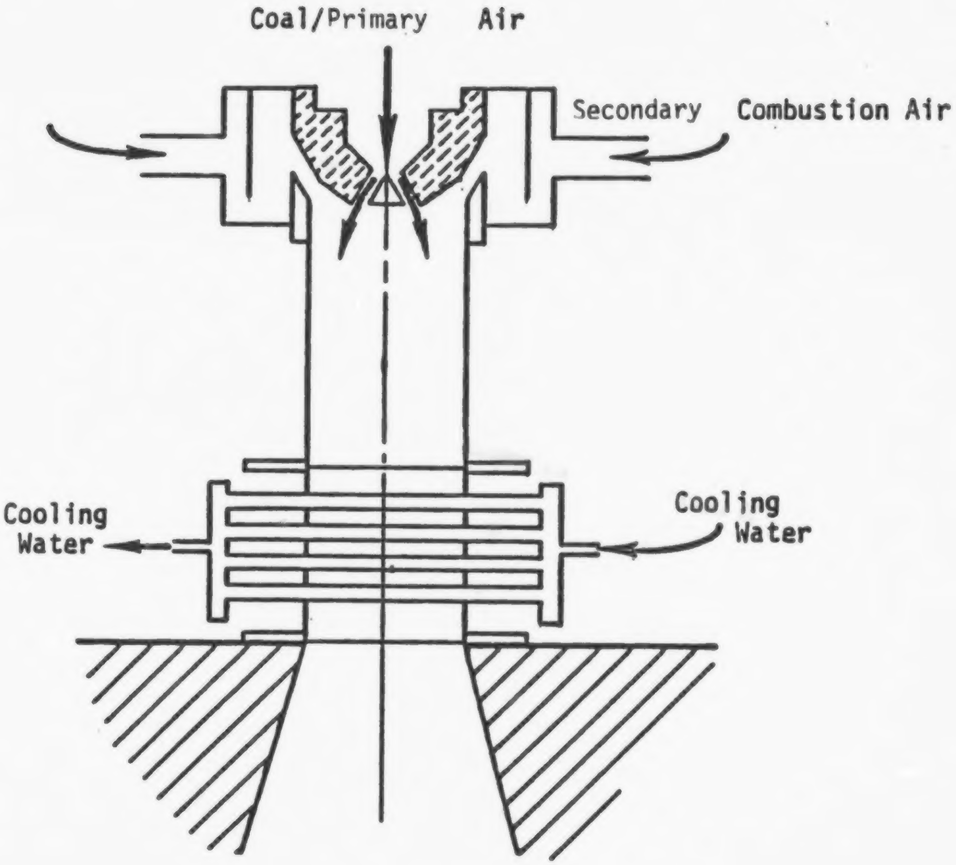

Coal/Primary Air
Secondary Combustion Air
Cooling Water
Cooling Water

Figure 5-5. Premixed burner.

the mixing chamber where the air and fuel are uniformly mixed. The premixed burner produced essentially a one-dimensional, plug-flow flame with no backmixing. Preignition of the fuel/air mixture in the mixing chamber was prevented by the cooling matrix located at the exit of the burner.

The furnace operating conditions for the test series were as follows:

- Primary Zone Stoichiometric Ratio (SR_1) - 0.8, 0.6.
- Overall Stoichiometric Ratio (SR_2) - 1.25.
- Firing Rate - 23.4 kW (80,000 Btu/hr), 17.6 kW (60,000 Btu/hr).
- Primary Zone Residence Time - 1.4 to 2.0 seconds.

Figure 5-6 presents measured temperature profiles in the CTT for each operating condition. The sorbent injection locations are designated. For each case, injection was performed through the same port, located 57.2 cm (22.5 inches) downstream from the burner.

Sorbent was transported into the furnace using pure nitrogen. A four hole, 45° injector was used to achieve rapid mixing between the sorbent and the furnace gas flow. The burnout air was introduced with an air ring that injected the air radially inward.

5.3 High Temperature Oven (HTO)

To study the interaction of sulfur with molten slags, the HTO facility presented in Figure 5-7 was designed and assembled. Gas mixtures of N_2, CO, CO_2 and H_2S were premixed and fed to the oven in a mixture approximately corresponding to Illinois coal flue gas at stoichiometric ratios of 0.5 and 0.7 (according to the NASA equilibrium code). The blended gas compositions are presented in Table 5-2. The electrical tube furnace had silicon-carbide heating elements to allow operation up to $1500^{\circ}C$ ($2732^{\circ}F$) throughout a 5.1 cm (2 inches) diameter, 30.5 cm (12 inches) long heated zone.

A high purity alumina tube was used for the reaction chamber. The tube extended out of the furnace to provide a cool-down region. Inside the

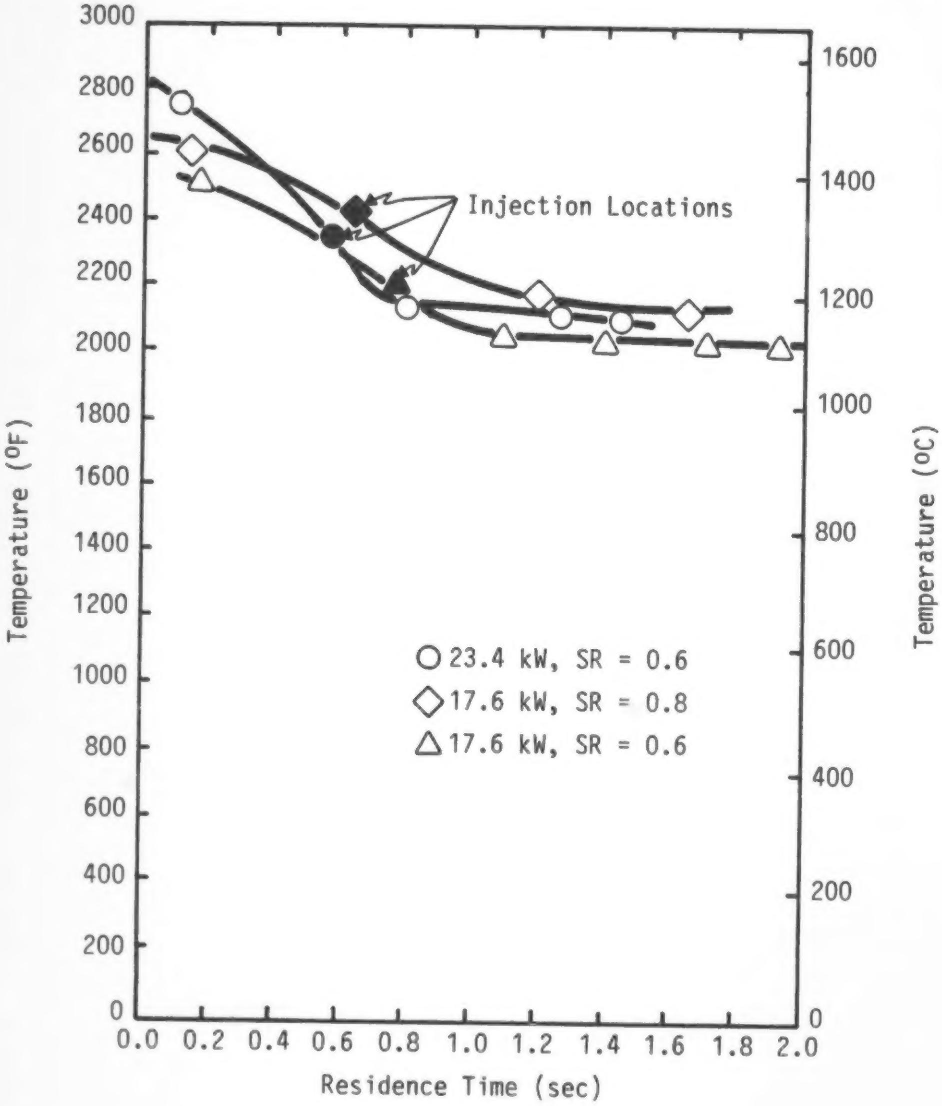


Figure 5-6. Temperature profiles measured in the fuel-rich zone of the CTT for three different operating conditions when burning Illinois coal.

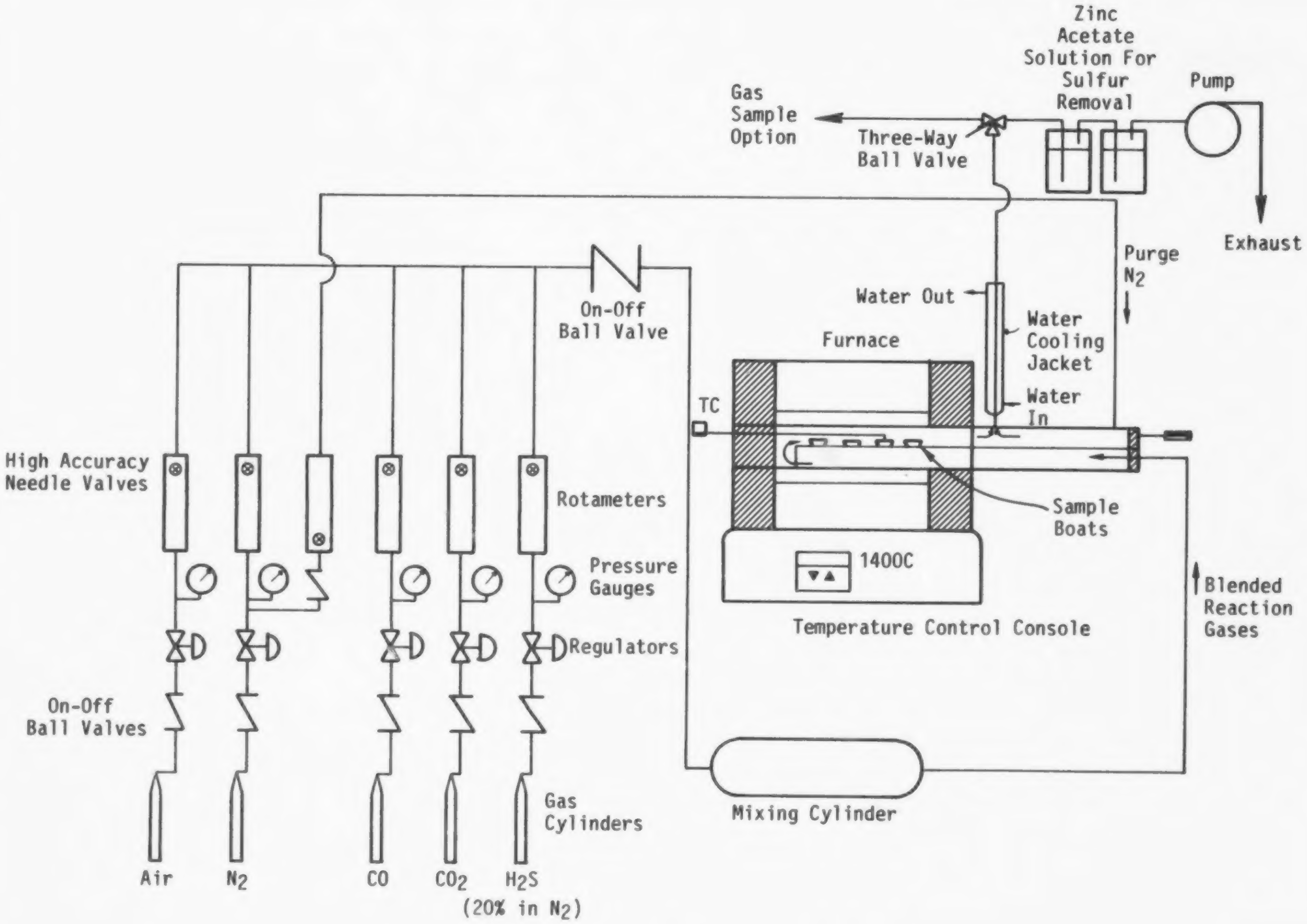

Gas Sample Option
Three-Way Ball Valve
Zinc Acetate Solution For Sulfur Removal
Pump
Exhaust
Purge N_2
Water Out
Water Cooling Jacket
Water In
Furnace
TC
Sample Boats
1400C
Temperature Control Console
Blended Reaction Gases
Mixing Cylinder
On-Off Ball Valve
High Accuracy Needle Valves
Rotameters
Pressure Gauges
Regulators
On-Off Ball Valves
Gas Cylinders
Air
N_2
CO
CO_2
H_2S (20% in N_2)

Figure 5-7. High temperature oven test facility with gas blending capability.

TABLE 5-2. HTO FEED GAS COMPOSITIONS

Stoichiometric Ratio	Gas Composition, Vol. Percent			
	N_2	CO	CO_2	H_2S
0.5	68.25	26.35	4.90	0.50
0.7	74.96	13.35	11.19	0.50

furnace tube was a dee-shaped alumina tube which formed a platform for ceramic sample boats to slide upon. The inside of the dee-shaped tube also provided a channel for preheating of the inlet gas before exposure to the slag samples. Nitrogen was used as the purge gas so that the samples cooled in an oxygen-free atmosphere.

Each ceramic sample boat held two smaller platinum boats made from 0.76 mm (0.003 inches) foil. The use of platinum was mandatory to prevent interaction between the slag samples and the constituents of the ceramic boats. The platinum was not completely inert. Iron in the slags attacked the platinum leaving a brittle, sometimes porous boat after a few tests.

The furnace temperature was maintained by a proportional-type controller. Temperature profiles were measured with and without a nitrogen flow of 2000 scc/min (4.2 scfh) through the reactor and are presented in Figure 5-8. The samples were positioned within a span of 12.7 cm (5 inches) in the reactor to assure a uniform temperature to within $\pm 10^{o}$C ($\pm 18^{o}$F).

Slag samples were prepared by preweighing required amounts of Illinois coal ash (ashed by ASTM procedures) CaO, CaS, or other additives.

5.4 Continuous Flue Gas Sampling System

Flue gas sampling was conducted in both the ITR and the CTT with a stainless-steel, water-cooled probe (jacketed with water cooling). The probe was capable (by inertial separation) of splitting the sorbent-laden sample gases into two streams. One stream was nearly particle-free to prevent additional sulfur reactions with sorbent within the probe. The other particle-laden stream was filtered downstream of the probe. The tip of this probe, called a phase discrimination probe, is shown in Figure 5-9.

The particle-laden sample stream was used to monitor O_2, CO, CO_2 and NO_x emissions. As shown in Figure 5-10, the sample stream was filtered, dried by passage through condensation traps and pumped to the analysis console. The gas species were continuously measured by the method indicated:

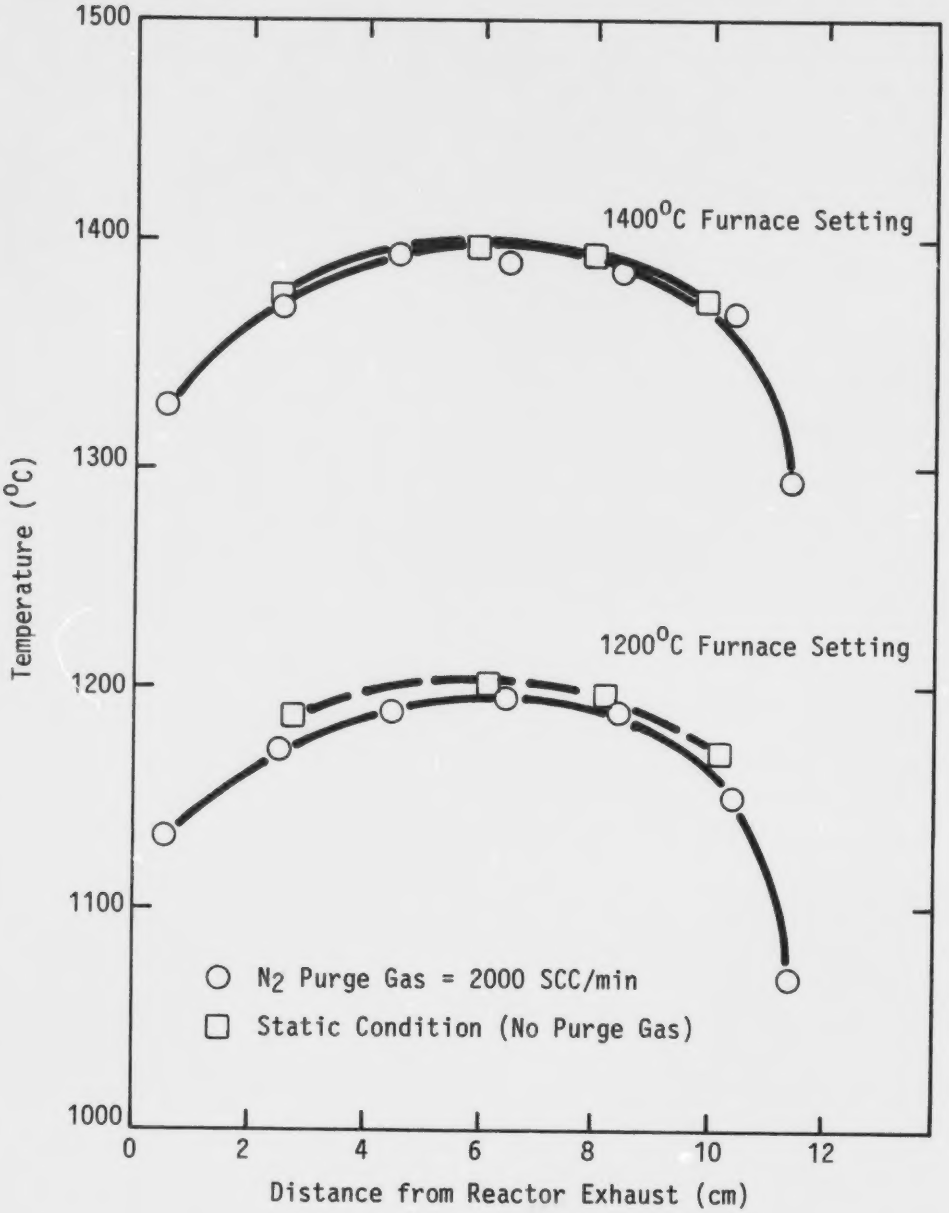


Figure 5-8. High temperature oven facility temperature distributions.

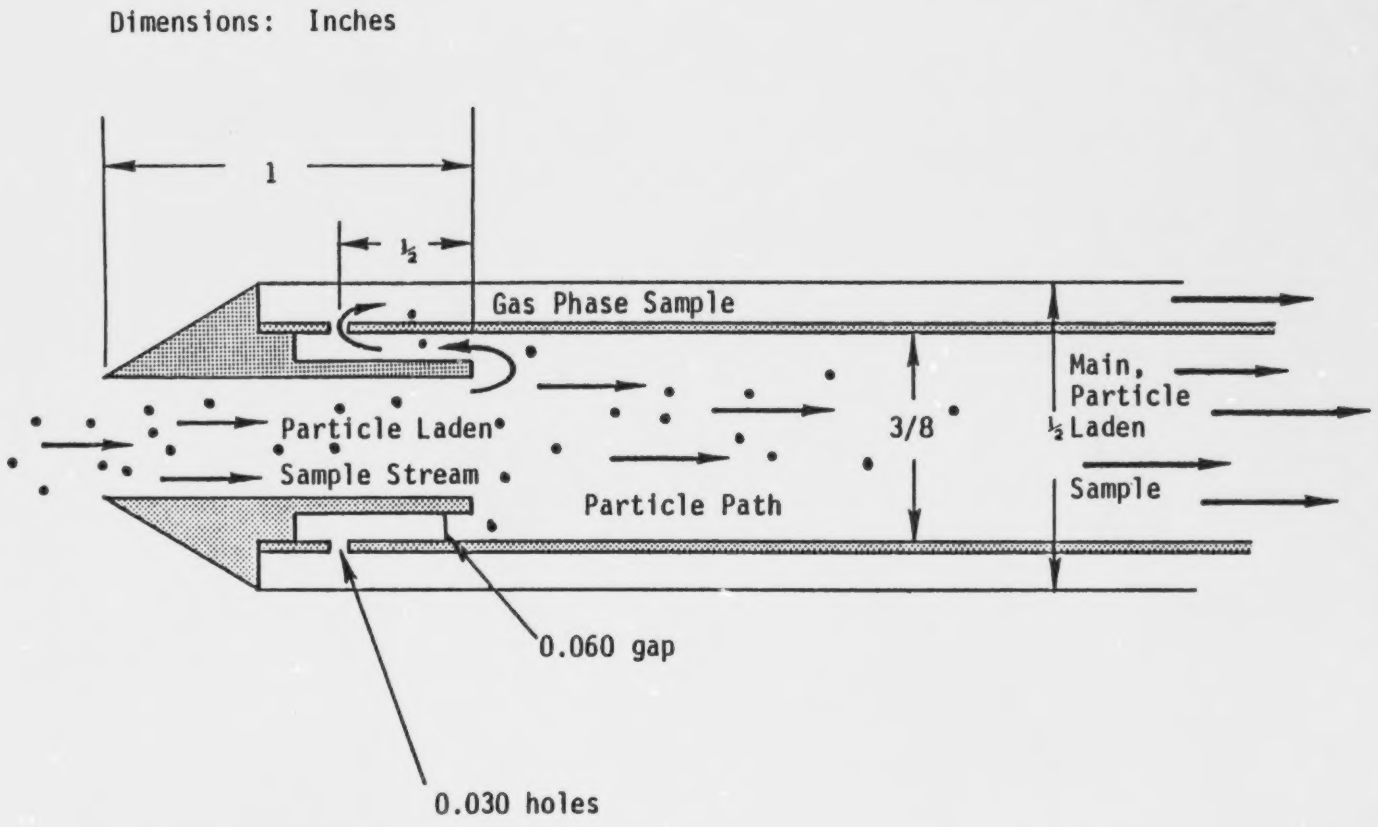

Dimensions: Inches
1
½
Gas Phase Sample
Particle Laden
Sample Stream
Particle Path
3/8
Main,
Particle
½ Laden
Sample
0.060 gap
0.030 holes

Figure 5-9. Phase discrimination probe tip.

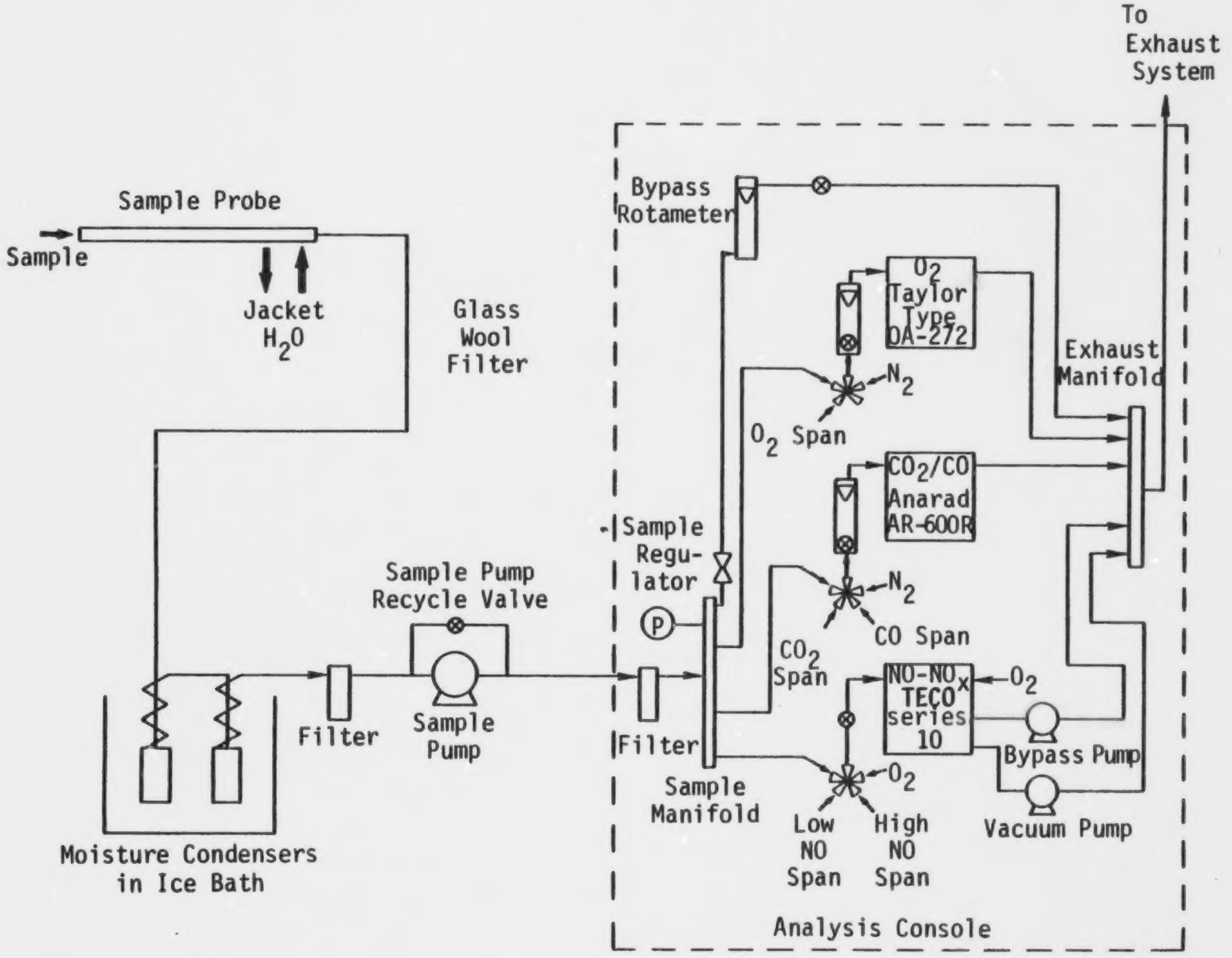

To
Exhaust
System
Sample Probe
Sample
Jacket
H_2O
Glass
Wool
Filter
Bypass
Rotameter
O_2
Taylor
Type
OA-272
Exhaust
Manifold
N_2
O_2 Span
CO_2/CO
Anarad
AR-600R
Sample
Regu-
lator
Sample Pump
Recycle Valve
N_2
CO Span
P
CO_2
Span
NO-NO_x
TECO
series
10
O_2
Filter
Sample
Pump
Filter
Bypass Pump
Sample
Manifold
O_2
Low
NO
Span
High
NO
Span
Vacuum Pump
Moisture Condensers
in Ice Bath
Analysis Console

Figure 5-10. Continuous monitoring flue gas sampling system.

- O_2 - paramagnetic
- CO/CO_2 - nondispersive infrared
- NO_x - chemiluminescent

The particle-free sample stream was used to monitor SO_2 emissions. The sample was transferred through a heated sample line and filter to a permeation tube dryer before being fed to a nondispersive ultraviolet analyzer (see Figure 5-11). The dryer selectively removed water from the gas stream by contacting the wet gas with a tubular membrane which was permeable to water. Sampling moist gases in this manner enabled a dry sample stream to be produced without the possibility of water condensation and sulfuric acid formation.

5.5 Reduced Sulfur Species Sampling System

To measure reduced sulfur species such as H_2S, COS and CS_2 (as well as SO_2) by gas chromatography, the same sample train system was used as for continuous SO_2 sampling except that the dry sample stream was fed to a tedlar sample bag rather than the ultraviolet SO_2 analyzer (see Figure 5-11). The collected sample was then transported to the EER chemistry lab for immediate (within two hours) analysis in a Perkin Elmer $\Sigma 2$ Gas Chromatograph equipped with a flame photometric detector and a Supelco Chromosil 310 column.

5.6 Solid Sampling Techniques

On the ITR, solid samples were collected with the probe presented in Figure 5-12. The probe was designed for isokinetic operation in the ITR facility. The sample was rapidly quenched upon entry into the probe in order to prevent further sulfidation reactions to occur. The design includes two water-cooled zones for better quench control without formation of condensation within the probe.

Solids sampling on the CTT did not require as long a probe as on the ITR since sampling was performed through side ports rather than through the exhaust. The system used is shown in Figure 5-13. Very high sample rates

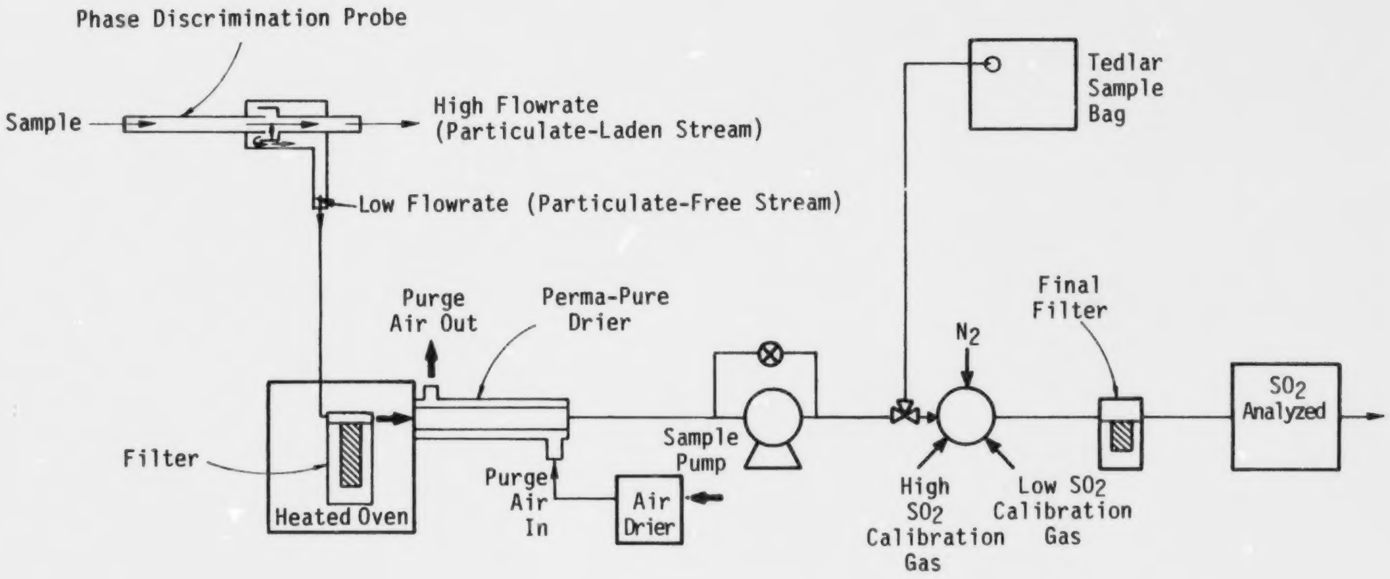

Phase Discrimination Probe
Sample
High Flowrate
(Particulate-Laden Stream)
Low Flowrate (Particulate-Free Stream)
Tedlar
Sample
Bag
Purge
Air Out
Perma-Pure
Drier
Final
Filter
N_2
SO_2
Analyzed
Filter
Heated Oven
Purge
Air
In
Air
Drier
Sample
Pump
High
SO_2
Calibration
Gas
Low SO_2
Calibration
Gas

Figure 5-11. SO_2 continuous monitoring and batch sampling system.

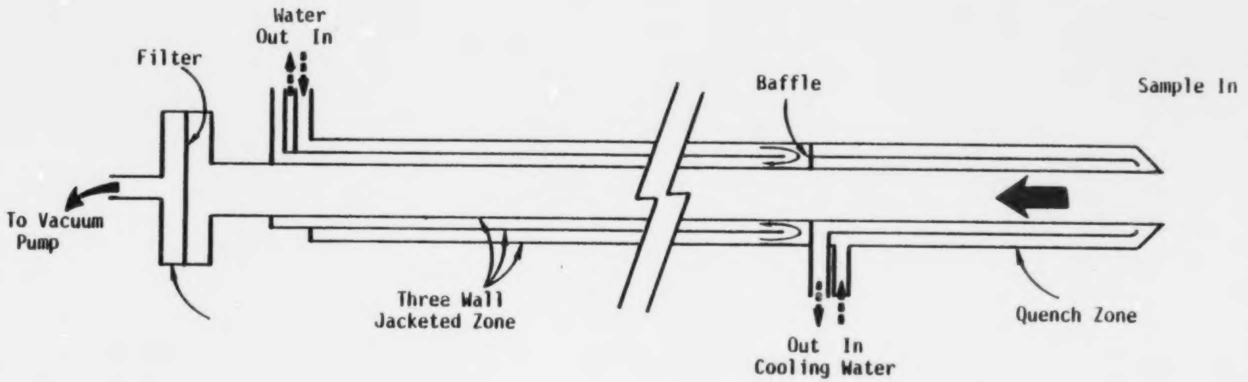

Water
Out In
Filter
Baffle
Sample In
To Vacuum Pump
Three Wall Jacketed Zone
Out In
Cooling Water
Quench Zone

Figure 5-12. Isokinetic solids sampling probe with upper and lower cooling jackets used in the ITR.

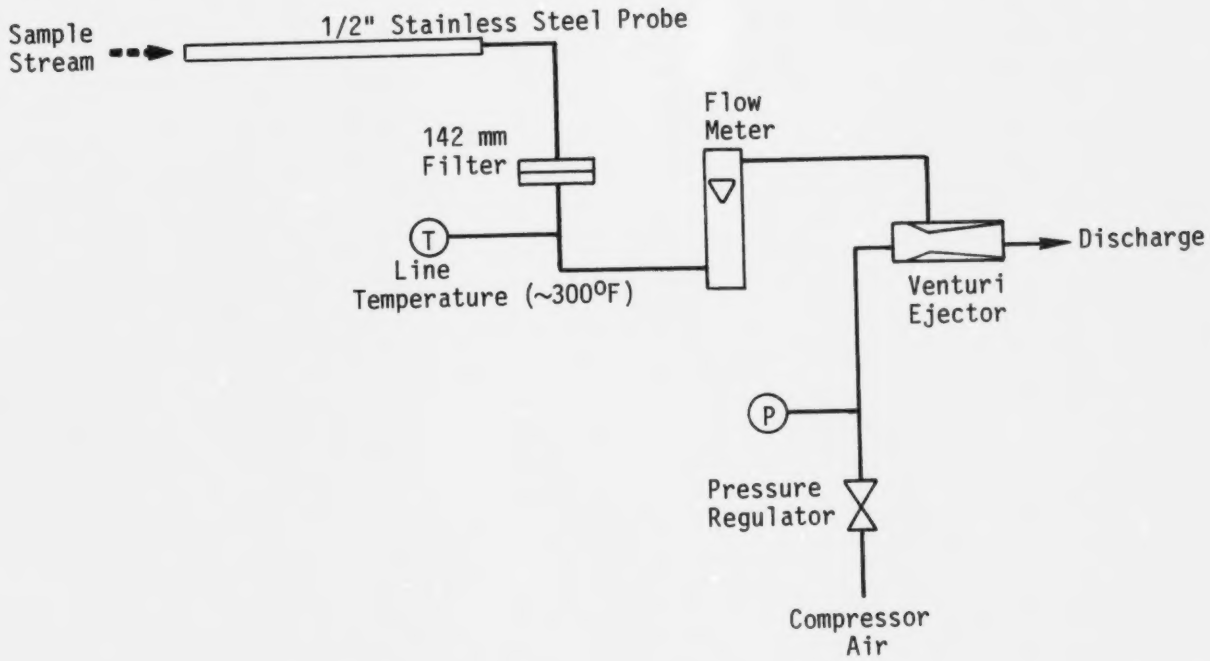

Sample Stream
1/2" Stainless Steel Probe
142 mm Filter
Flow Meter
T
Line Temperature (~300°F)
Venturi Ejector
Discharge
P
Pressure Regulator
Compressor Air

Figure 5-13. Solid sampling system used on the CTT.

were used through a hot probe to avoid long probe residence times and to maintain a hot sample stream. A thermocouple behind the sample filter was used to assure moderate temperatures that remained above the dew point.

5.7 Sorbent Feeding

For both the ITR and CTT facilities, sorbent was fed using an Accurate Model 300 solids displacement feeder. Features of the feeder include variable speed replaceable augers and a flexing vinyl hopper to avoid material bridging. The dry sorbent was transported to each furnace using dry nitrogen.

5.8 Temperature Measurement

Gas temperatures were measured in the ITR using a fine-wire thermocouple to minimize radiation losses. The thermocouple was made with 0.025 mm diameter type-S thermocouple wire, butt-welded across a forked support. Figure 5-14 presents a diagram of the fine-wire thermocouple.

In the CTT, where more room was available, gas temperatures were measured with a B-type thermocouple in a suction pyrometer jacket as shown in Figure 5-15. The pyrometer was placed in the flue gas stream with the opening in the alumina sheath pointing downstream. A sufficient gas sample was drawn around the thermocouple tip such that the convective heat transfer of the gas to the thermocouple dominated over the radiation heat loss of the thermocouple tip to the surroundings.

5.9 Test Material Compositions

For the entrained flow sulfidation tests, the sorbents used were Linwood atmospheric hydrate and Vicron 45-3 carbonate. Compositions of the two sorbents are presented in Table 5-3 and their size distributions are presented in terms of cumulative weight percent in Figure 5-16. Both of these sorbents are commercially available and have been investigated in fuel-lean sulfidation studies.

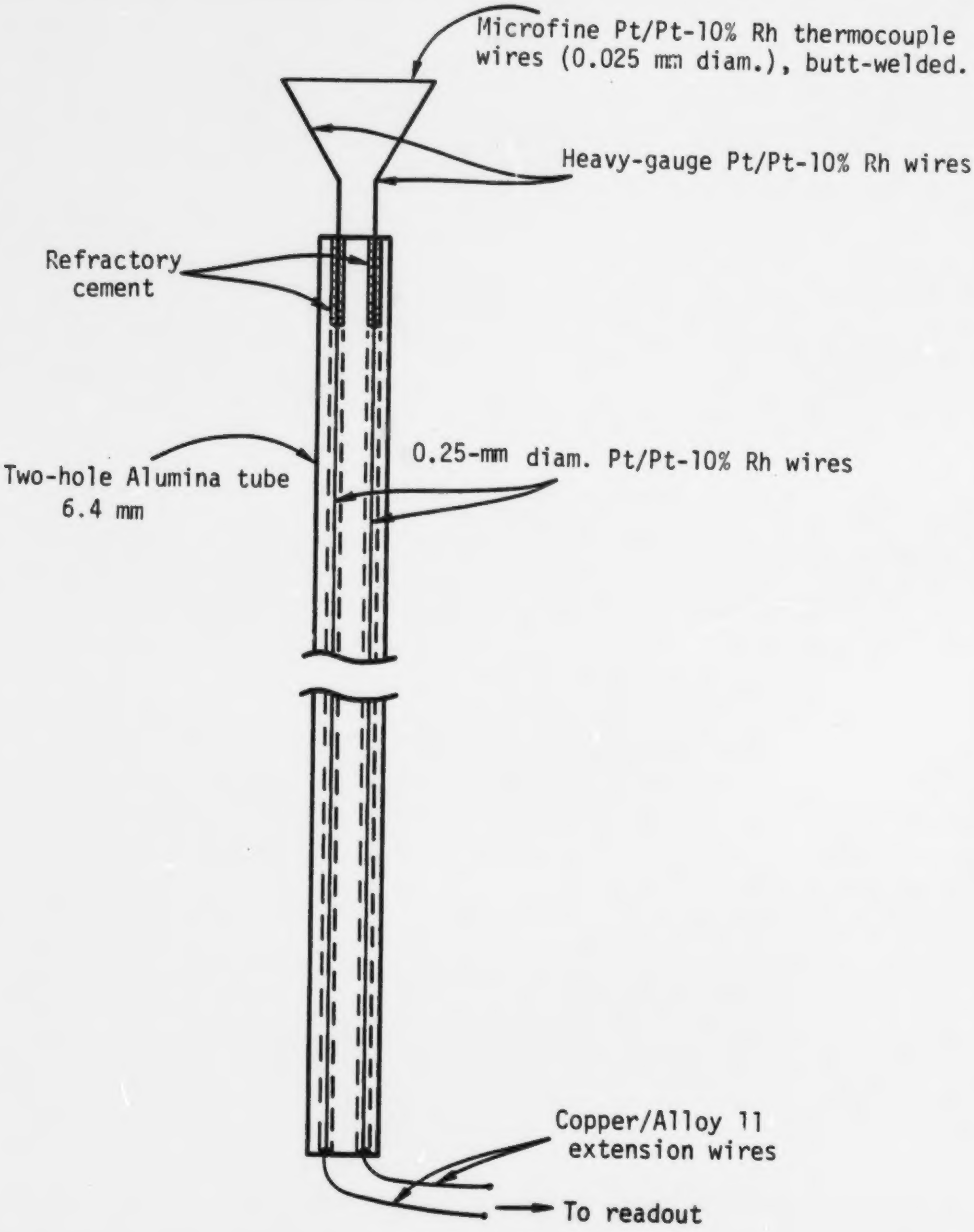

Microfine Pt/Pt-10% Rh thermocouple wires (0.025 mm diam.), butt-welded.
Heavy-gauge Pt/Pt-10% Rh wires
Refractory cement
Two-hole Alumina tube 6.4 mm
0.25-mm diam. Pt/Pt-10% Rh wires
Copper/Alloy 11 extension wires
To readout

Figure 5-14. Fine-wire thermocouple probe for gas temperature measurements in the ITR.

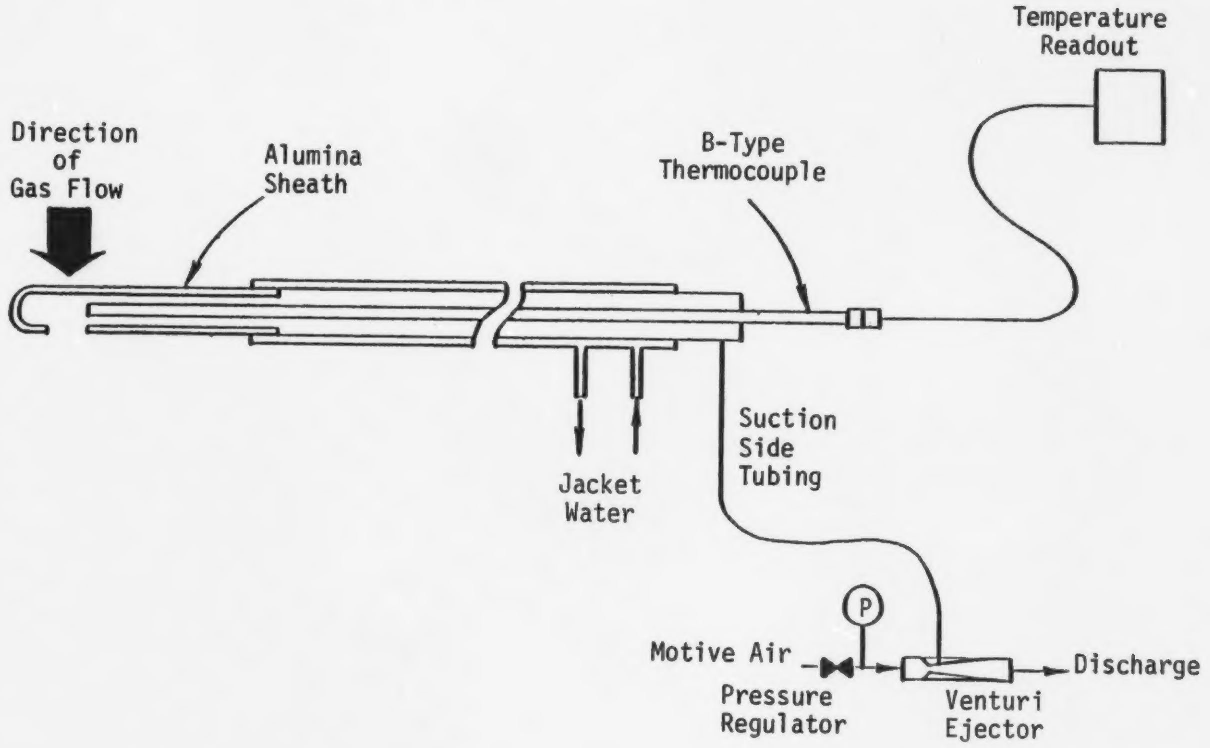

Direction of Gas Flow
Alumina Sheath
B-Type Thermocouple
Temperature Readout
Suction Side Tubing
Jacket Water
P
Motive Air
Pressure Regulator
Venturi Ejector
Discharge

Figure 5-15. Gas temperature measurement system for the CTT.

TABLE 5-3. PROPERTIES OF VICRON LIMESTONE AND LINWOOD ATMOSPHERIC HYDRATE

Sorbent	Vicron Limestone	Linwood Atmospheric Hydrate
Surface Area (m^2/gm)	0.7	16.0
Median Particle Size (μm)	9.8	2.2
Ca (weight %)	39.2	51.6
Mg	0.33	0.97
Na	0.01	0.00
K	0.01	0.00
Fe	0.06	0.27
Si	0.09	0.66
Al	0.02	0.18

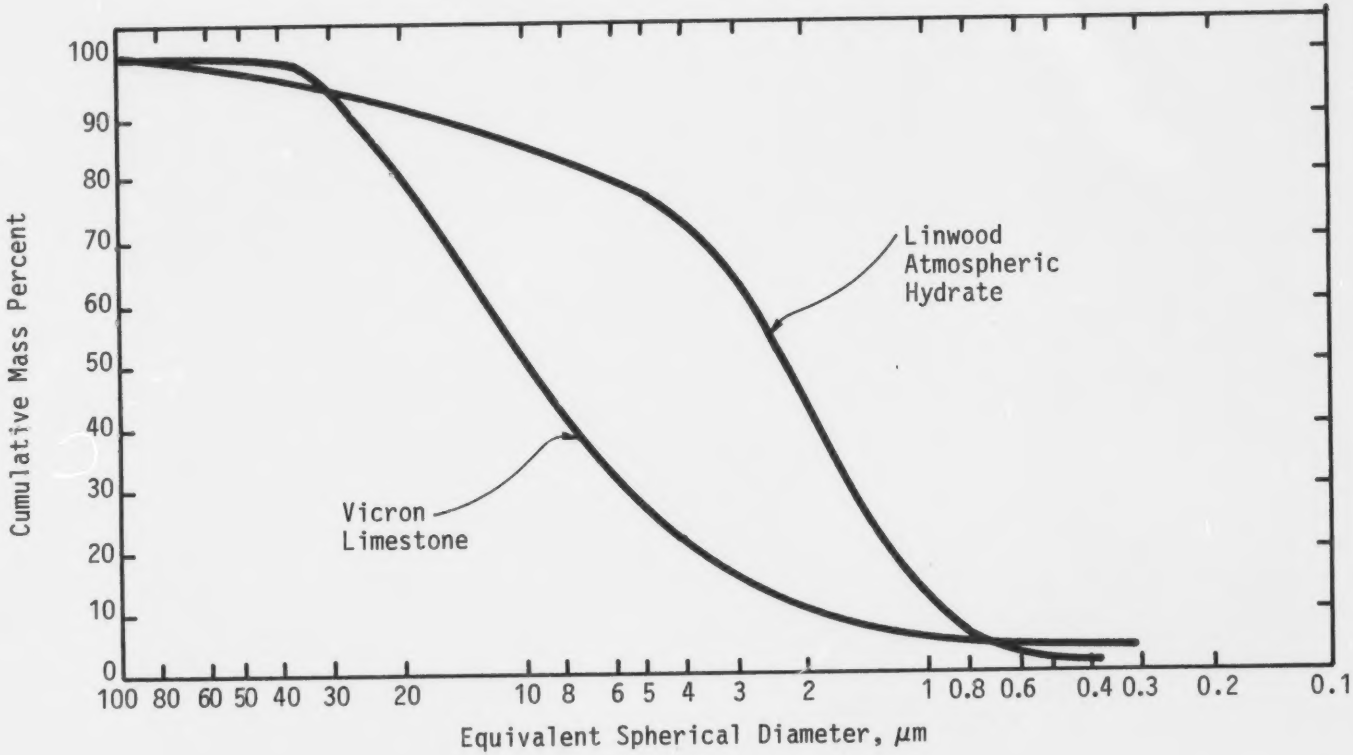


Figure 5-16. Comparison of sorbent size distributions as measured by x-ray sedigraph technique.

The Illinois coal used for the entrained flow tests is a high sulfur, high slagging, eastern coal commonly used in cyclone combustors. Its composition is presented in Table 5-4.

For the slag tests performed in the static oven facility, Illinois coal ash was obtained from the same Illinois coal as used in the entrained flow studies. The coal was ashed by ASTM specified procedure (in air at 750^{o} C (1382^{o}F)). Table 5-5 presents the mineral analysis of the ash.

Additives used to mix with the ash included CaO (97.3 percent pure), CaS (97.0 percent), MgO (95.0 percent), Fe_2O_3 (100 percent), P_2O_5 (99.7 percent), B_2O_3 (98.9 percent), and CaF_2 (99 percent). Table 5-6 presents the calculated mineral distribution for mixtures corresponding to coal firing with Ca/S molar ratios of 0.5, 1.0 and 2.0 and Fe/S of 1.0, 2.0, 4.0, 2.55 (with 15.1 percent MgO added) and 4.4 (the last two were tested for direct comparison to reported results by DeYoung, 1984).

TABLE 5-4. ILLINOIS COAL COMPOSITION AND HEATING VALUE

Ultimate Analysis (wt%, dry)	
Carbon	69.52
Hydrogen	4.98
Nitrogen	1.33
Sulfur	3.84
Oxygen	10.71
Chlorine	0.12
Ash	9.50

Proximate Analysis (wt%, as received)	
Moisture	7.92
Ash	8.75
Volatiles	38.46
Fixed Carbon	44.87

Higher Heating Value (dry)

29,602 kJ/kg (12,726 Btu/lb)

TABLE 5-5. MINERAL ANALYSIS OF ILLINOIS COAL ASH

Mineral (wt %, dry)	
SiO_2	47.93
Al_2O_3	16.73
Fe_2O_3	17.37
MgO	1.11
CaO	4.67
Na_2O	1.02
K_2O	2.21
TiO_2	0.94
P_2O_5	0.14
SO_3	4.11
MnO	0.03
Others	3.74
Total	100.00
Molar Basicity	0.27

TABLE 5-6. COMPOSITIONS OF CaO/ASH AND Fe_2O_3/ASH MIXTURES

Ca/S (molar ratio)	0.5	1.0	2.0	--	--	--	--	--
Fe/S (molar ratio)	--	--	--	1.0	2.0	4.0	2.55	4.4
CaO/Ash (wt. ratio)	0.31	0.66	1.37	--	--	--	--	--
Fe_2O_3/Ash (wt. ratio)	--	--	--	0.83	1.84	3.85	2.39	4.26
Molar Basicity	0.83	1.48	2.77	0.8	1.45	2.75	3.08	3.01
SiO_2 (wt %)	36.43	28.55	19.92	26.14	16.87	9.87	12.31*	9.11
Al_2O_3	12.72	9.96	6.95	4.12	5.89	3.45	4.38	3.18
Fe_2O_3	13.20	10.35	7.22	54.93	70.91	82.98	65.94	84.30
MgO	0.84	0.66	0.46	0.61	0.39	0.23	13.12	0.21
CaO	26.89	42.14	58.81	2.55	1.64	0.96	1.20	0.89
Na_2O	0.78	0.61	0.42	0.56	0.36	0.21	0.26	0.19
K_2O	1.68	1.32	0.92	1.21	0.78	0.46	0.57	0.42
TiO_2	0.71	0.56	0.39	0.51	0.33	0.19	0.24	0.18
P_2O_5	0.11	0.08	0.06	0.08	0.05	0.03	0.04	0.03
SO_3	3.12	2.45	1.71	2.24	1.45	0.85	1.06	0.78
MnO	0.02	0.02	0.01	0.02	0.01	0.00	0.00	0.00
Others	3.5	3.3	3.13	2.04	1.32	0.77	0.96	0.71
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

*15.1% by weight of Fe_2O_3/ash mixture added as MgO

6.0 ENTRAINED FLOW SULFIDATION RESULTS

To investigate the free-stream reaction of calcium-based sorbents with reduced species of sulfur (H_2S and COS), sorbent was injected into an isothermal, fuel-rich exhaust stream in the ITR facility. The sulfur concentration was controlled by the doping of H_2S either with the gaseous fuel or downstream of the flame zone. This facility was ideal for precise control of stoichiometry, temperature and gas phase residence time. Gas phase sampling and analysis using gas chromatography allowed determination of the sulfur speciation.

Gradual sulfur evolution from coal firing adds another level of complexity to the process. The evolution of sulfur from coal and its subsequent reaction with calcium-based sorbents was investigated in the CTT facility. The CTT was operated with a slow temperature quench rate to approximately simulate the free-stream thermal environment within a precombustor. Again, gas chromatography was used to establish gas phase sulfur speciation as the sulfur evolved from the coal. Solid sampling and analysis allowed determination of specie (C, S, H, N) evolution rates and provided an independent check on sulfidation.

6.1 Isothermal -- Gas-Fired

6.1.1 Fuel Effects

Before attempting to determine the effectiveness of calcium sulfidation as a sulfur removal process from sulfur laden, fuel-rich exhaust streams, it was of critical importance to establish the sulfur speciation within the ITR reactor environment. It was found that the use of different gaseous fuel types impacted the sulfur speciation and indirectly effected the measured calcium utilization. Two fuels were tested, methane (CH_4) and ethylene (C_2H_4). Each was doped with enough H_2S to generate 5000 ppm of sulfur in the reactor. Figure 6-1 shows the difference in sulfur speciation for the two fuels at a temperature of 1100^oC (2012^oF) and stoichiometric ratio of 0.83. The methane flame exhaust sulfur speciation was mostly H_2S (about 50

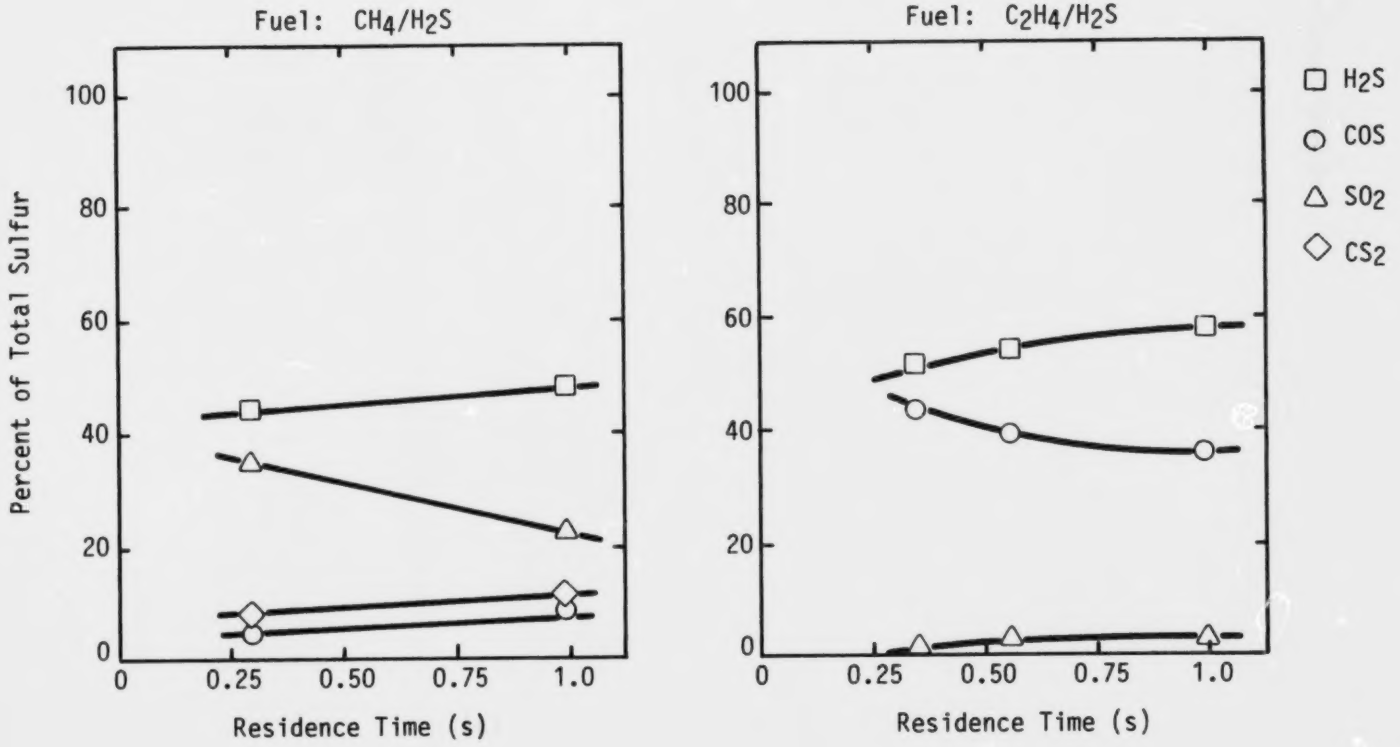


Figure 6-1. Sulfur speciation in the ITR at 1100°C, SR = 0.83 when doping CH_4 and C_2H_4 with approximately 5000 ppm H_2S.

percent), but had substantial amounts of SO_2 and CS_2. The ethylene flame provided about the same amount of H_2S but substantially higher COS and little measurable SO_2 or CS_2.

As shown in Figure 6-2, the sulfur speciation had an impact on calcium utilization. The larger amount of H_2S and COS present in the ethylene flame case resulted in a slightly higher calcium utilization due to the availability of the sulfur compounds which support sulfidation.

The sulfur speciation for both of these cases were far from expected based on equilibrium calculations. It is believed that under fuel-rich operating conditions on the ITR that a delayed flame front exists. The high peak temperatures and large radical specie concentrations that exist in the flame front produces a non-equilibrium sulfur speciation at the entrance of the reactor. As the exhaust gases travel through the reactor, the sulfur speciation slowly moves towards equilibrium (see Figure 6-1).

Ethylene is a "faster" fuel than methane producing a distribution of sulfur species at the reactor entrance which were closer to equilibrium. In addition, a new burner was utilized with the ethylene which more effectively held the flame to the burner.

There was, in fact, some visual evidence that the methane flame sporadically licked into the reactor zone. This also produced unsteadiness in the sulfur speciation.

6.1.2 Impact of H_2S Injection Location

To avoid the problems of shifting sulfur speciation, the dopant H_2S was injected downstream of the ethylene flame. This method produced a very high, steady H_2S concentration throughout the reactor. Figure 6-3 compares sulfur speciation when H_2S was premixed with the ethylene to downstream H_2S doping. Figure 6-4 shows that the capture levels using Linwood atmospheric hydrate are higher for the case of higher H_2S concentration. Even though the total reduced sulfur concentration (H_2S-plus-COS) is the same, it is believed that

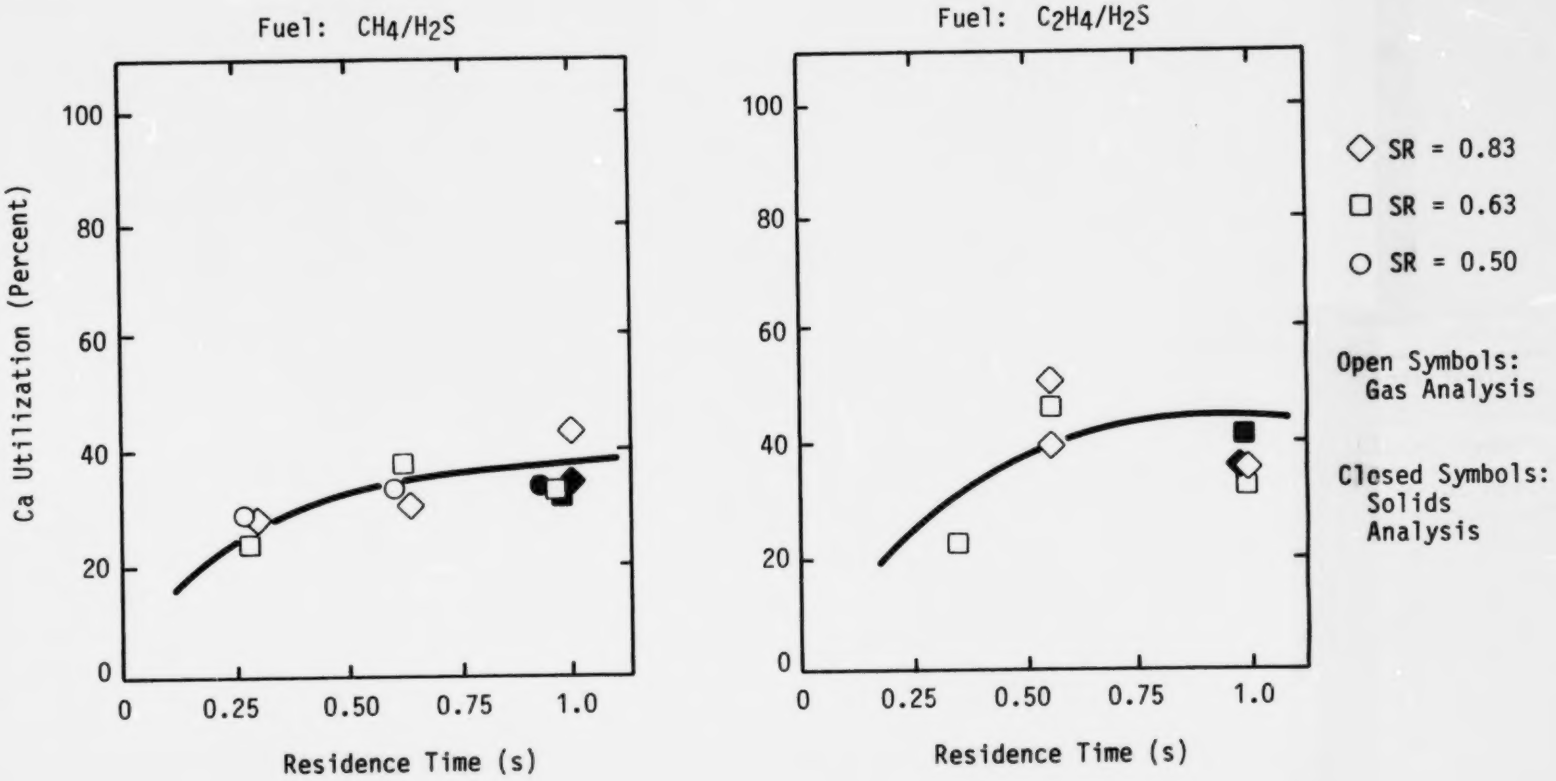


Figure 6-2. Calcium utilization in the ITR using Linwood atmospheric hydrate, measured by both gas and solids analysis. ITR held at 1100°C when doping CH_4 and C_2H_4 with 5000 ppm H_2S ($Ca/S \simeq 1.0$ for each case).

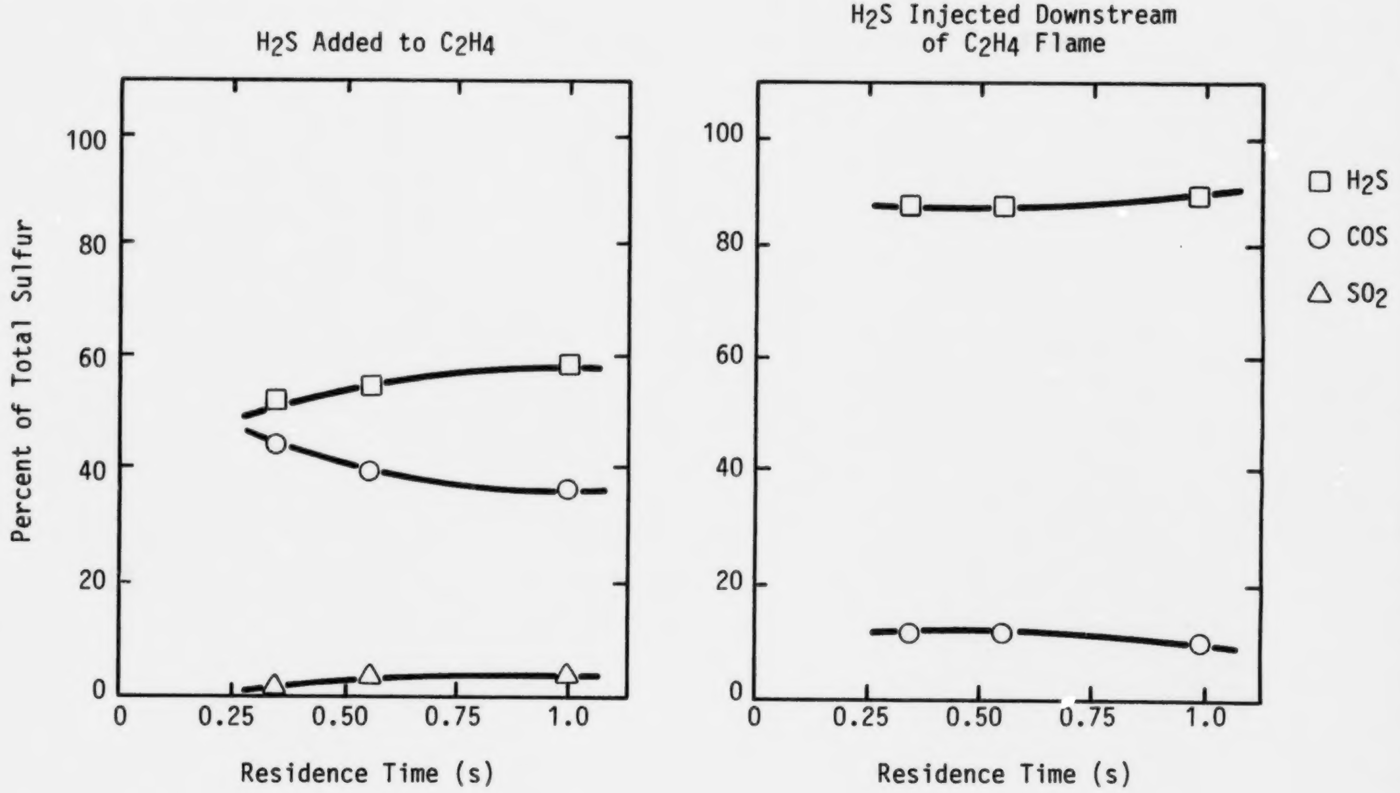


Figure 6-3. Sulfur speciation in the ITR at 1100°C, SR = 0.83 when either mixing 5000 ppm H_2S with the fuel (C_2H_4) or injecting it downstream of the flame.

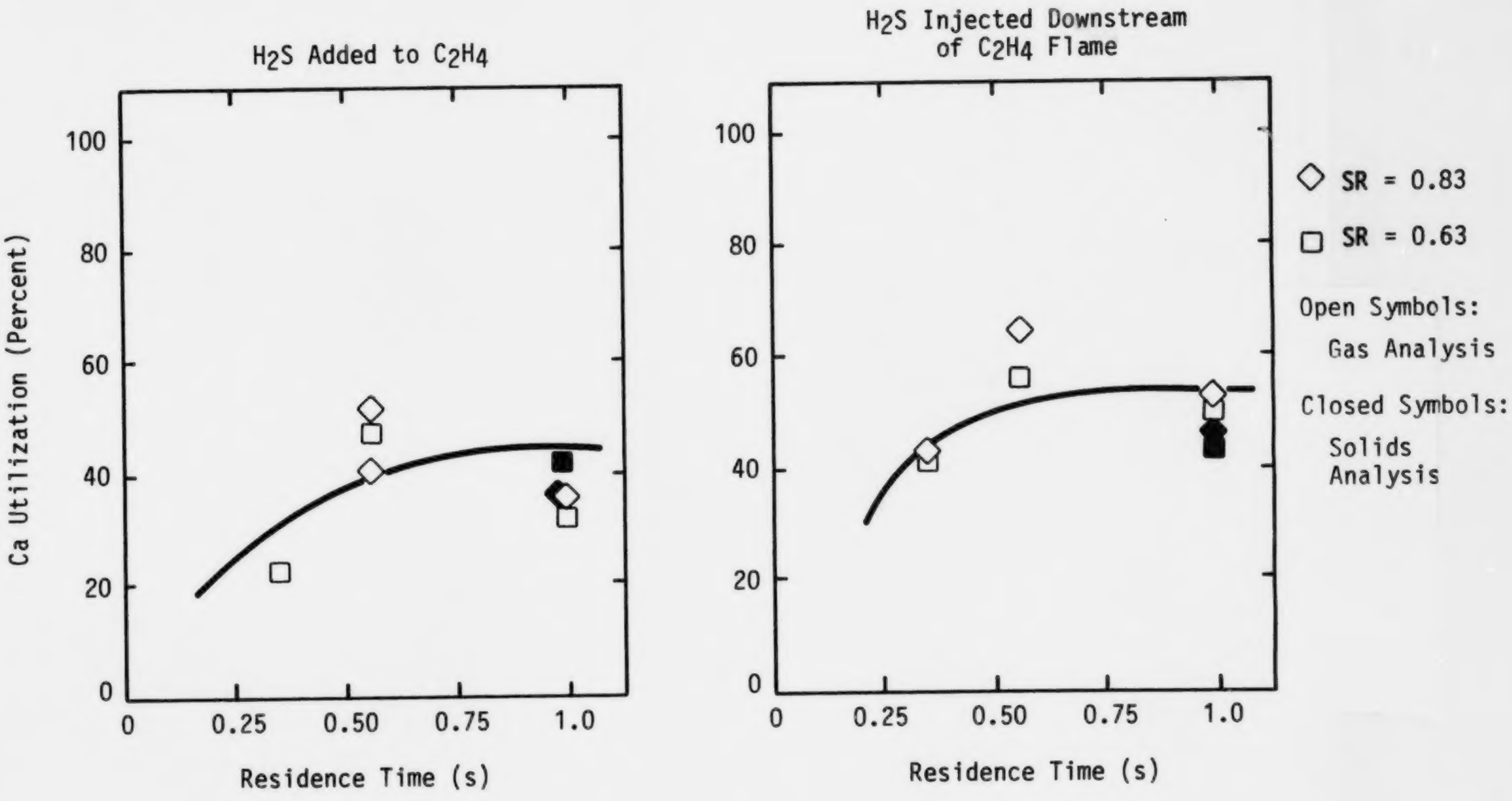


Figure 6-4. Calcium utilization in the ITR using Linwood atmospheric hydrate, measured by both gas and solid analysis. ITR held at 1100°C when doping the fuel (C_2H_4) with 5000 ppm H_2S or injecting it downstream of the flame ($Ca/S \simeq 1.0$ for each case).

the kinetics of sulfidation and sorbent sintering favors the higher H_2S concentration. Borgwardt et al. (1984a) have shown that the reaction rate for H_2S and CaO reaction is about three times as high as the COS and CaO reaction. Within similar residence times, this would favor the higher H_2S concentration. In addition, Borgwardt has shown that the reactivity of the sorbent is reduced with time due to thermal sintering. Therefore, the case of higher COS concentration would provide more time for thermal sintering to occur resulting in lower capture levels.

One other complexity that must be considered is the shifting of sulfur species upon the depletion of H_2S. As Figure 6-5 shows, the measured relative speciation when sorbent was injected was similar to that measured before sorbent was injected. This suggests that there was a shift in speciation from COS to H_2S as the H_2S pool was depleted.

6.1.3 Time-Resolved Capture

The capture data presented in Figures 6-2 and 6-4 were obtained at various reactor residence times by adjusting the gas phase sample probe along the length of the reactor. In all cases, the capture appears to be dominated by events that occur early in the reactor. It is believed that the sorbent is most reactive shortly after calcination and quickly losses reactivity as available reaction sites are used up and as the thermal sintering process reduces specific surface area. Once an external product layer is produced, further reaction is limited by product layer diffusion. These results emphasize the importance of the thermal conditions and sulfur speciation that exist early in a precombustor.

6.1.4 Stoichiometry Effects

In the ITR facility, the sulfur was introduced as a gaseous dopant so that sulfur evolution was not an issue. The speciation was dominated by non-equilibrium influences, such as proximity of the flame front to the reactor entrance. Because of these factors, the flame stoichiometry only had a strong impact on sulfur speciation when it altered flame conditions for the

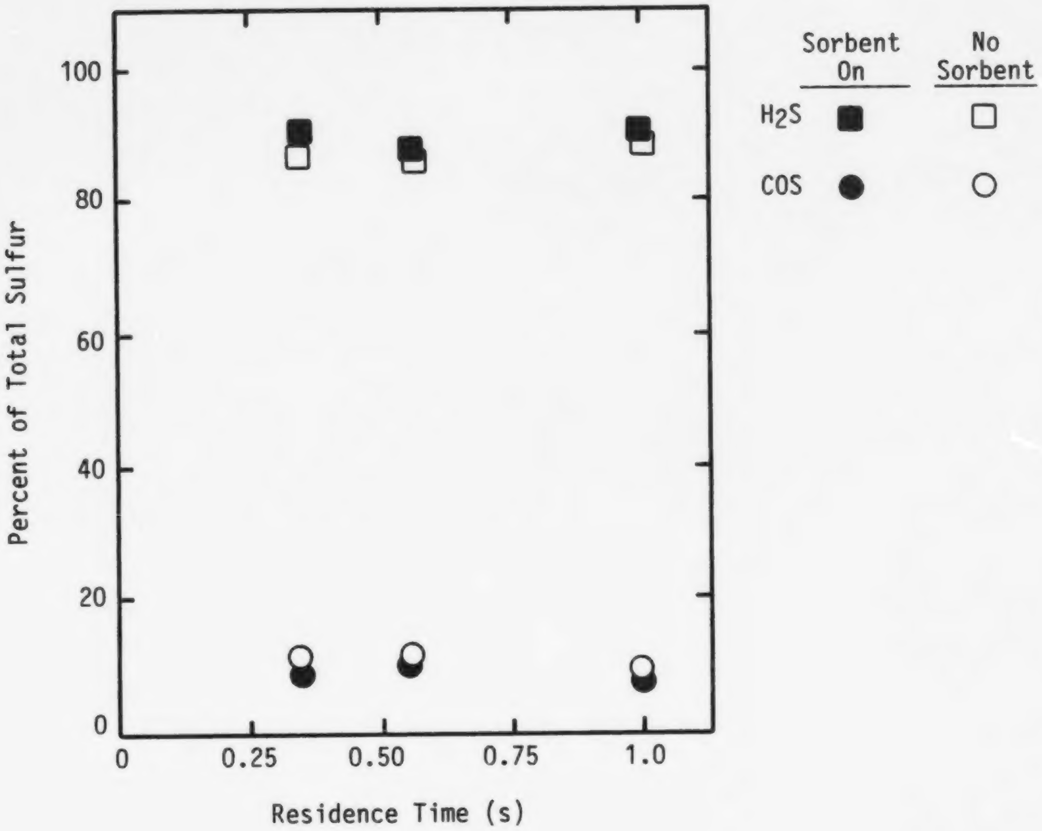


Figure 6-5. Sulfur speciation with and without sorbent present in the ITR at 1100°C, SR = 0.83. 5000 ppm H_2S injected downstream of C_2H_4 flame. Sorbent was Linwood atmspheric hydrate at Ca/S ≃ 1.0.

cases where H_2S was doped with the fuel. For the cases when H_2S was injected downstream of the flame, the concentration distribution did not vary with stoichiometry, as shown in Figure 6-6. Figures 6-2 and 6-4 showed earlier that sulfur capture levels were similar as stoichiometry was varied from SR = 0.83 to 0.63.

6.1.5 Temperature Effects

An important issue facing the use of calcium-based sorbents in practical precombustor systems is the allowable temperature range in which the process is effective. Figure 6-7 shows that an increase in reactor temperature from 1100°C (2012°F) to 1300°C (2372°F) only slightly shifted the sulfur speciation towards lower H_2S and higher COS concentrations. However, calcium utilization was significantly reduced at the elevated temperature as shown in Figure 6-8. It is believed that the high temperature significantly increases sorbent sintering so that a much less reactive material is available for sulfidation. At temperatures above 1100°C, the specific surface area of sorbents has been shown to diminish significantly (Cole et al., 1985b). Thus, operating temperatures in high firing density, slagging precombustors may be too high to achieve optimum calcium utilization.

6.1.6 Impact of Sorbent Type

Linwood atmospheric hydrate was chosen as the baseline sorbent due to its high reactivity so that the impact of changing parameters could be identified by the capture data. From an economic standpoint the performance of an inexpensive calcium carbonate ($CaCO_3$) is of interest. A common limestone, Vicron 45-3, was tested in the ITR giving the capture results presented in Figure 6-9. Calcium utilization for the limestone was significantly lower than for the Linwood hydrate but high compared to Vicron when tested under fuel-lean, sulfation conditions. The relative capture levels when comparing Linwood to Vicron (i.e., their reactivity ranking) is similar under these fuel-rich sulfidation conditions to fuel-lean results on this facility and others (Cole et al., 1985a, EER, 1986, and Overmoe et al., 1986). This suggests that the ultimate entrained flow sulfidation will be

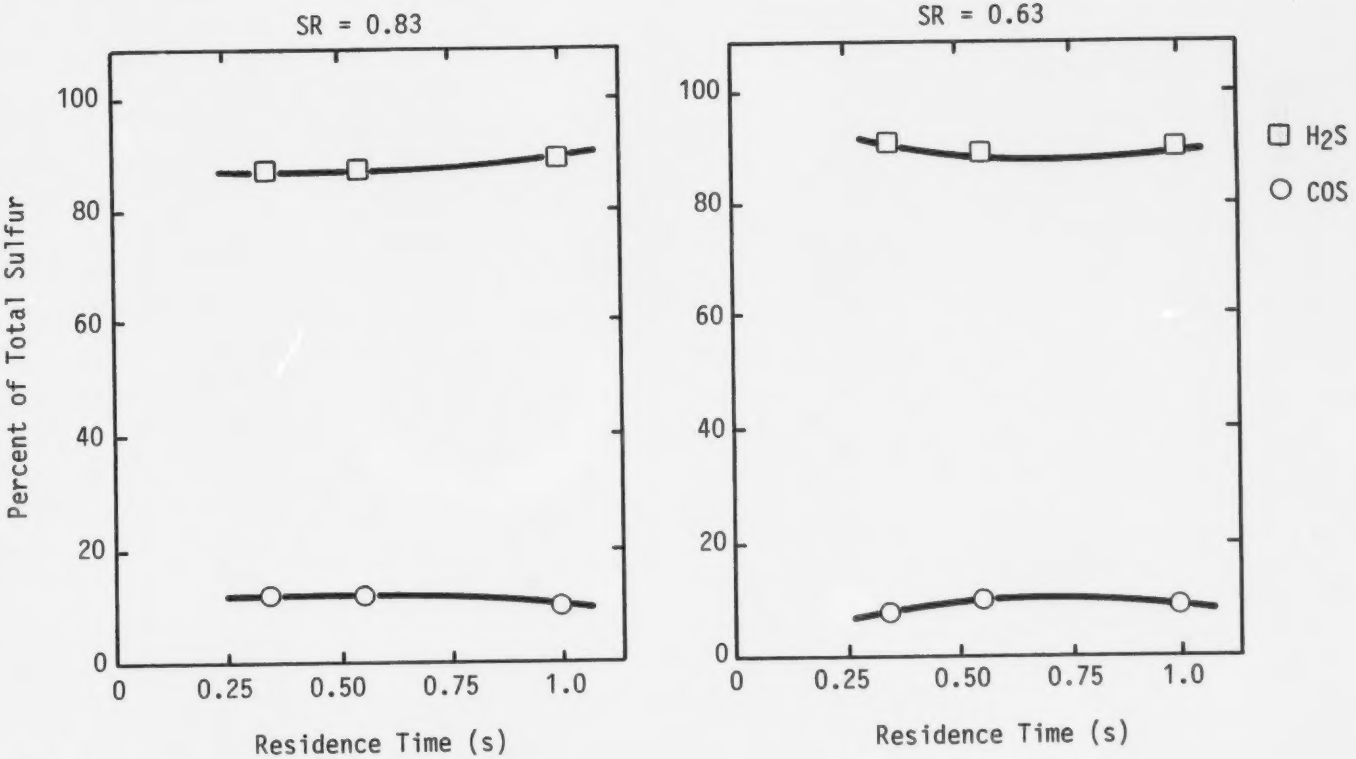


Figure 6-6. Sulfur speciation in the ITR at 1100°C when injecting 5000 ppm H_2S downstream of the C_2H_4 flame.

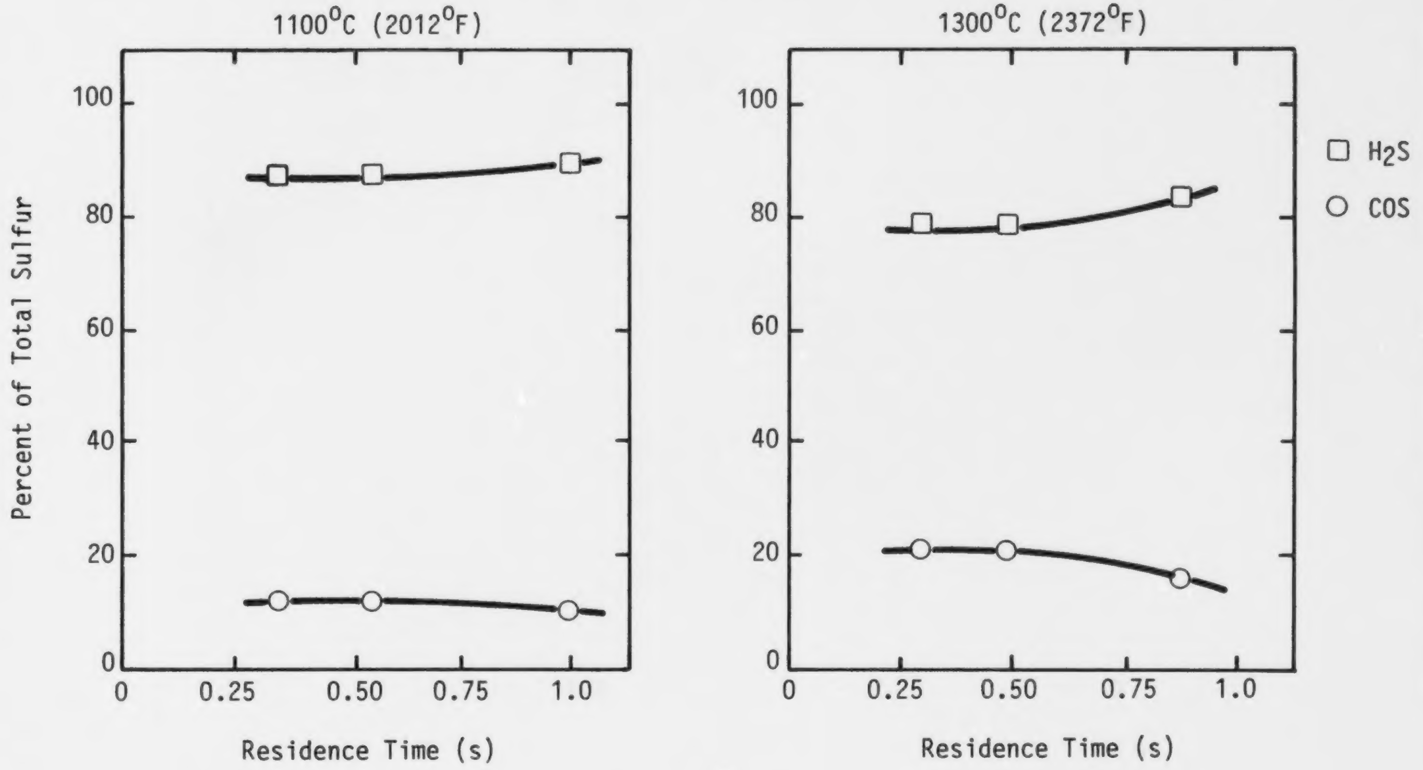


Figure 6-7. Sulfur speciation in the ITR at SR = 0.83 when injecting 5000 ppm H_2S downstream of the C_2H_4 flame.

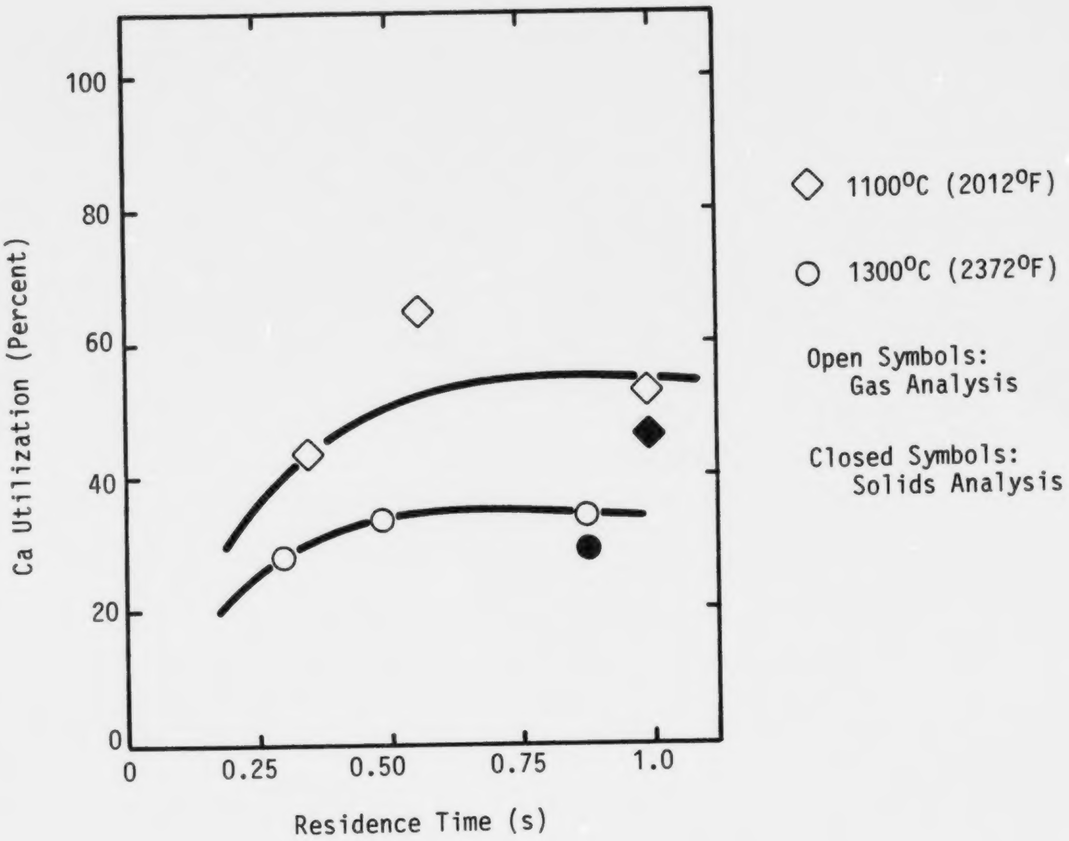


Figure 6-8. Calcium utilization in the ITR at SR = 0.83 when injecting 5000 ppm H_2S downstream of a C_2H_4 flame. Sorbent was Linwood atmospheric hydrate with Ca/S $\simeq$ 1.0 for each case.

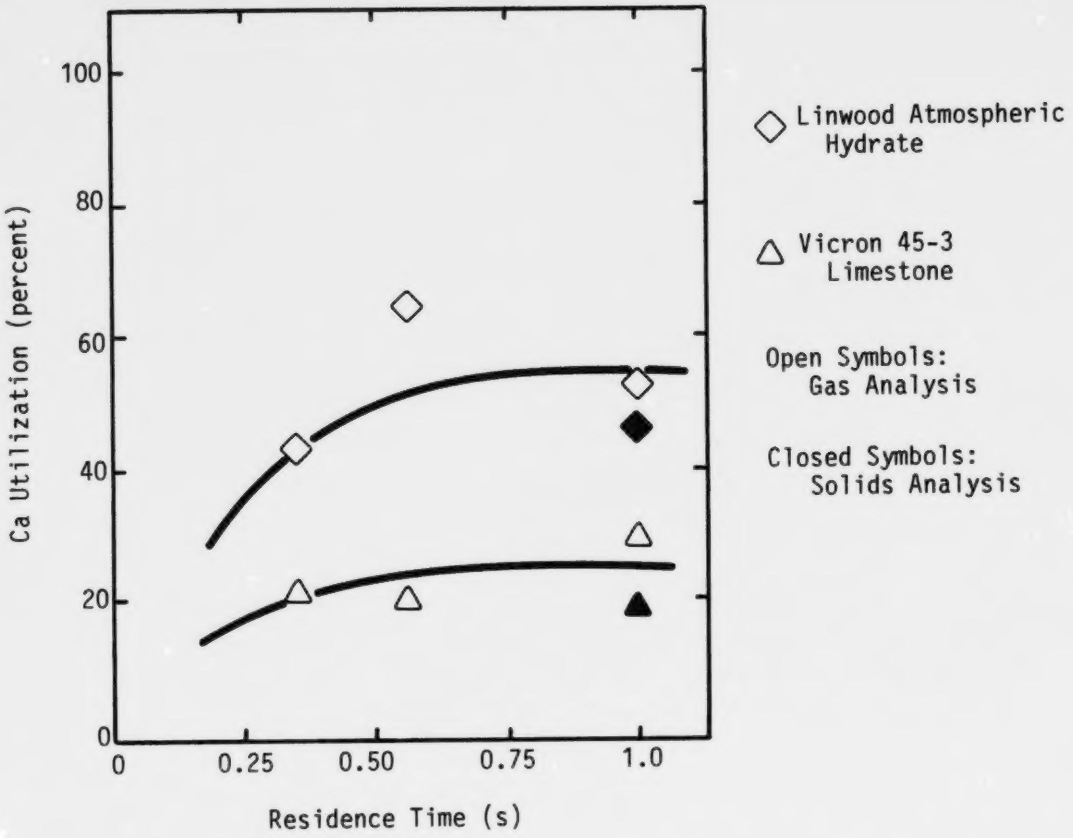


Figure 6-9. Calcium utilization in the ITR at 1100°C, SR = 0.83 with 5000 ppm H_2S injected downstream of the C_2H_4 flame. Both sorbents fed at Ca/S ≃ 1.0.

limited in application by the reactivity of the sorbent. Other studies on sorbent reactivity for fuel-lean sorbent utilization (Silcox et al., 1986) can provide useful information on the ranking of sorbent types and the optimum thermal environment for maximum calcium utilization.

6.1.7 Gas Phase Versus Solids Sampling

Under nearly every test condition, both gas phase and solid sampling was performed at the reactor exit to help validate the capture results. Figures 6-2, 6-4 and 6-8 show that the results were typically within 10 percent of each other; close enough to give support to any conclusions drawn from these results. The fact that the solids results are consistently lower than the gas phase results may be due to a small build-up of sorbent on the walls of the reactor which would cause a slight increase in gas phase capture but would not impact the sorbent that passed straight through the reactor and was collected by the solids sampling probe.

6.1.8 Comparison of Fuel-Rich to Fuel-Lean Capture

Figure 6-10 presents a comparison of calcium utilization for both Linwood hydrate and Vicron carbonate when tested under fuel-lean and fuel-rich conditions at similar temperatures. Even though the batch sampling technique used under fuel-rich conditions is less precise than the continuous SO_2 sampling system used for fuel-lean capture testing the substantial improvements in calcium utilization under fuel-rich conditions is unmistakable. Certainly the process holds promise as an effective sulfur reduction technique if the proven conditions can be reproduced in practical precombustor systems.

6.2 Slow Quench Rate -- Coal-Fired

To investigate the potential of fuel-rich sulfur capture under more realistic conditions, a coal-fired test series was initiated on the CTT. The CTT facility provided the opportunity to test carbon burnout and sulfur

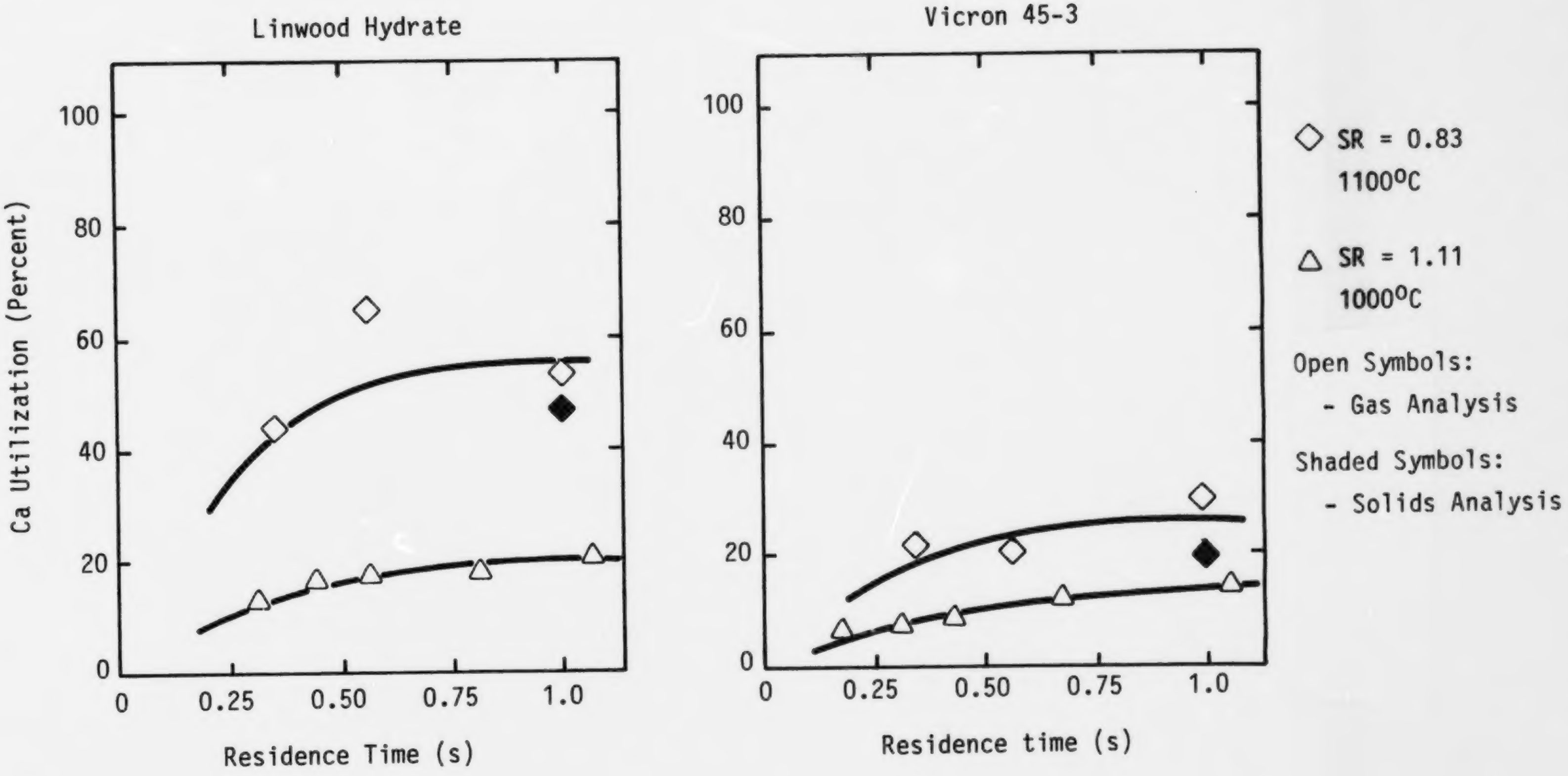


Figure 6-10. Calcium utilization in the ITR under fuel-rich and fuel-lean conditions for both Linwood atmospheric hydrate and Vicron 45-3 limestone.

evolution from coal under fuel-rich conditions at the same time as evaluating the sulfidation reaction.

6.2.1 Stoichiometry Effects

The CTT was operated at two stoichiometric ratios, 0.8 and 0.6. A stoichiometric ratio of 0.8 was considered optimum for practical precombustor operation in terms of NO_x control and favorable carbon utilization. A level of 0.6 was established as a reasonable lower limit for operation of a precombustor system.

Figure 6-11 presents a comparison of sulfur speciation along the reactor length. Clearly operation at SR = 0.8 was not acceptable since less than 30 percent of the input sulfur was in the form of H_2S and COS over a majority of the reactor residence time. However, operation at SR = 0.6 made approximately 70 percent of the gas phase sulfur available as H_2S and COS for reaction with CaO.

As expected, capture levels for the SR = 0.6 case are substantially higher than at SR = 0.8 due to the availability of the reduced sulfur species for reaction with the sorbent. Figure 6-12 shows the substantial benefits of operation at SR = 0.6. Practical precombustor systems which promote fast and efficient evolution of sulfur from coal along with speciation that favors H_2S and COS would be more likely to give higher sulfur capture using calcium-based sorbents.

The evolution of carbon and other species for both stoichiometries are shown in Figure 6-13. Evolution of hydrogen, nitrogen and sulfur were similar for the two cases while consumption of carbon lagged behind noticeably for the SR = 0.6 case. At the richer stoichiometry, only 70-75 percent of the carbon evolved while around 90 percent of the carbon evolved at SR = 0.8 by the end of the reaction zone. This emphasizes one of the important practical issues facing sulfur control in precombustors - can high carbon utilization be achieved at the extreme fuel-rich stoichiometries required for sulfur capture? Extended residence times by deposition and

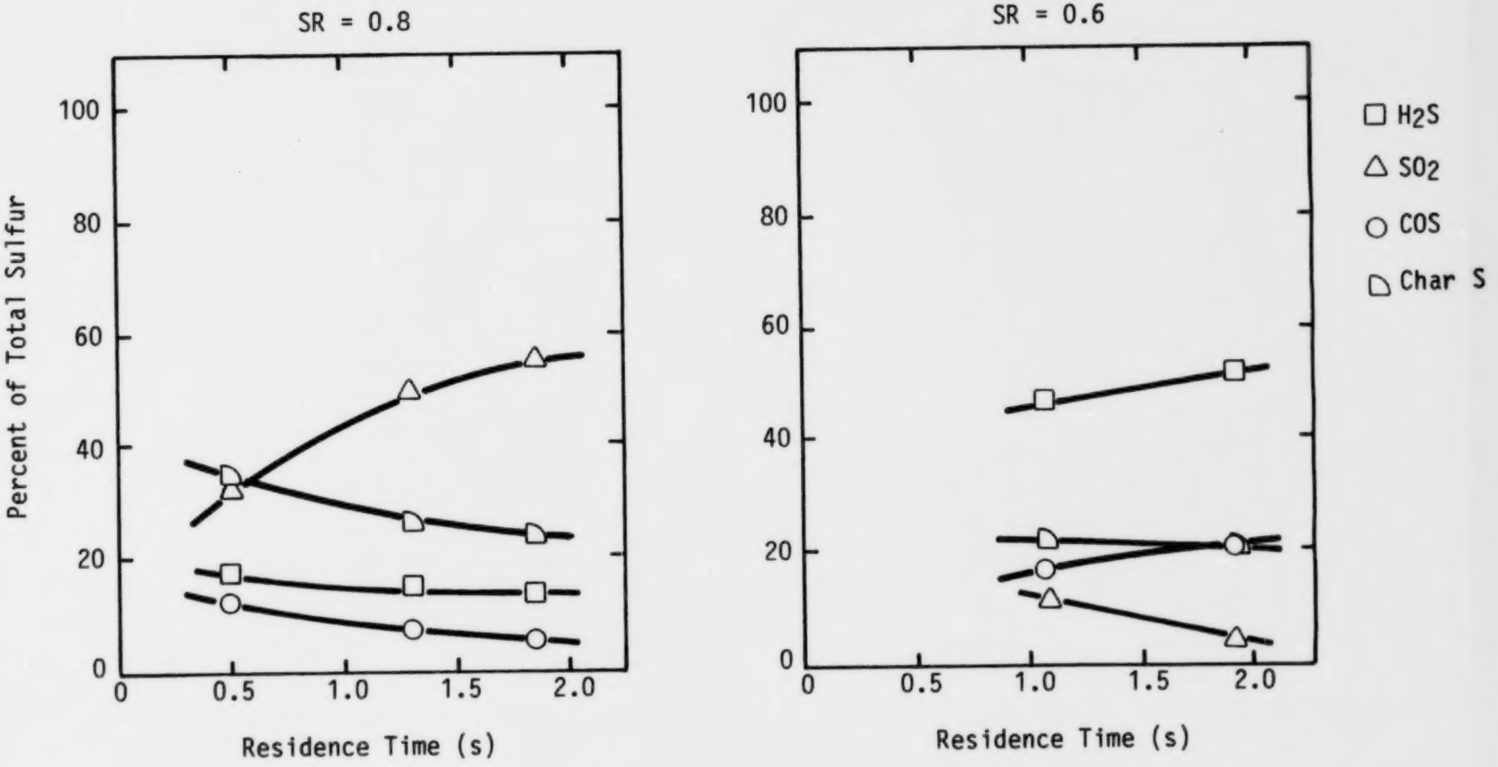


Figure 6-11. Sulfur speciation in the CTT firing Illinois coal at 17.6 kW (60,000 Btu/hr).

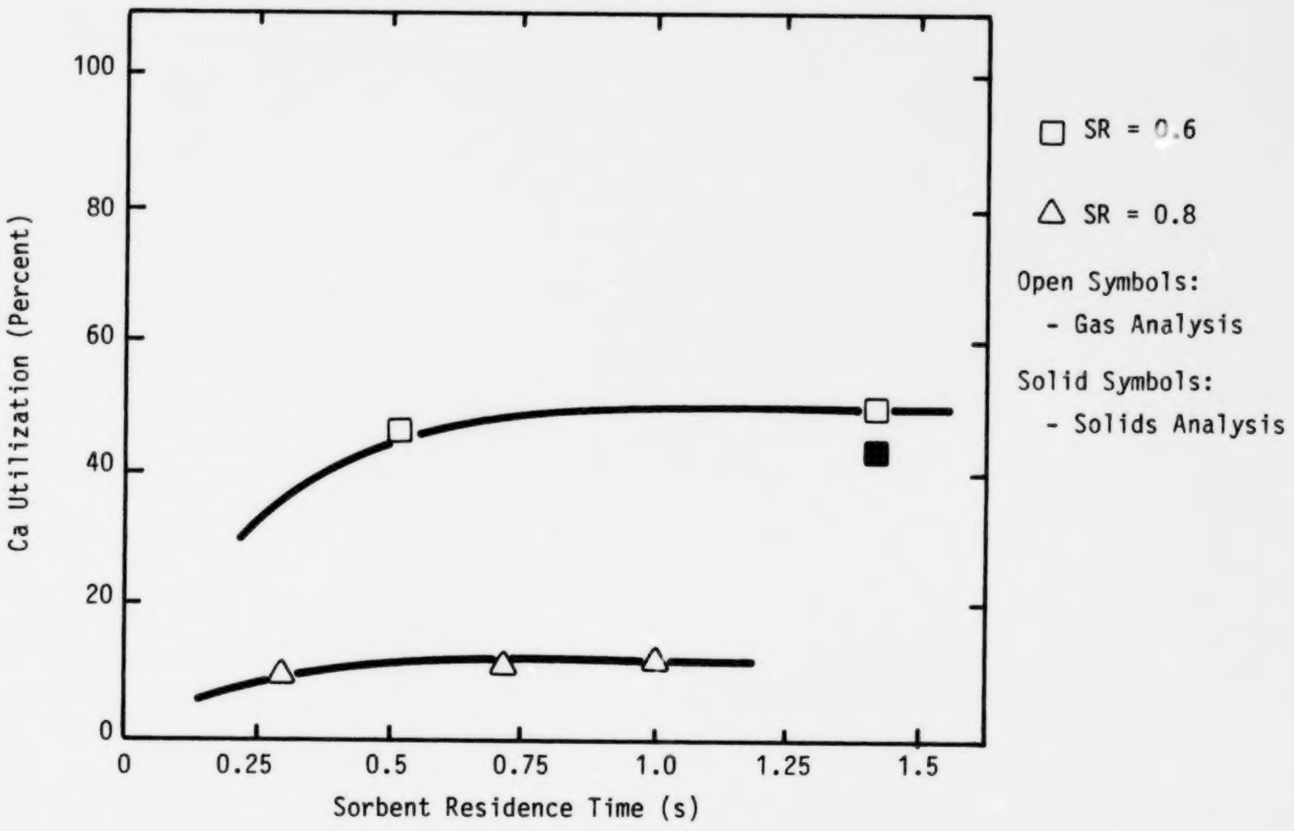


Figure 6-12. Calcium utilization in the CTT firing Illinois coal at 17.6 kW (60,000 Btu/hr), injecting Linwood atmospheric hydrate at about Ca/S = 1.0.

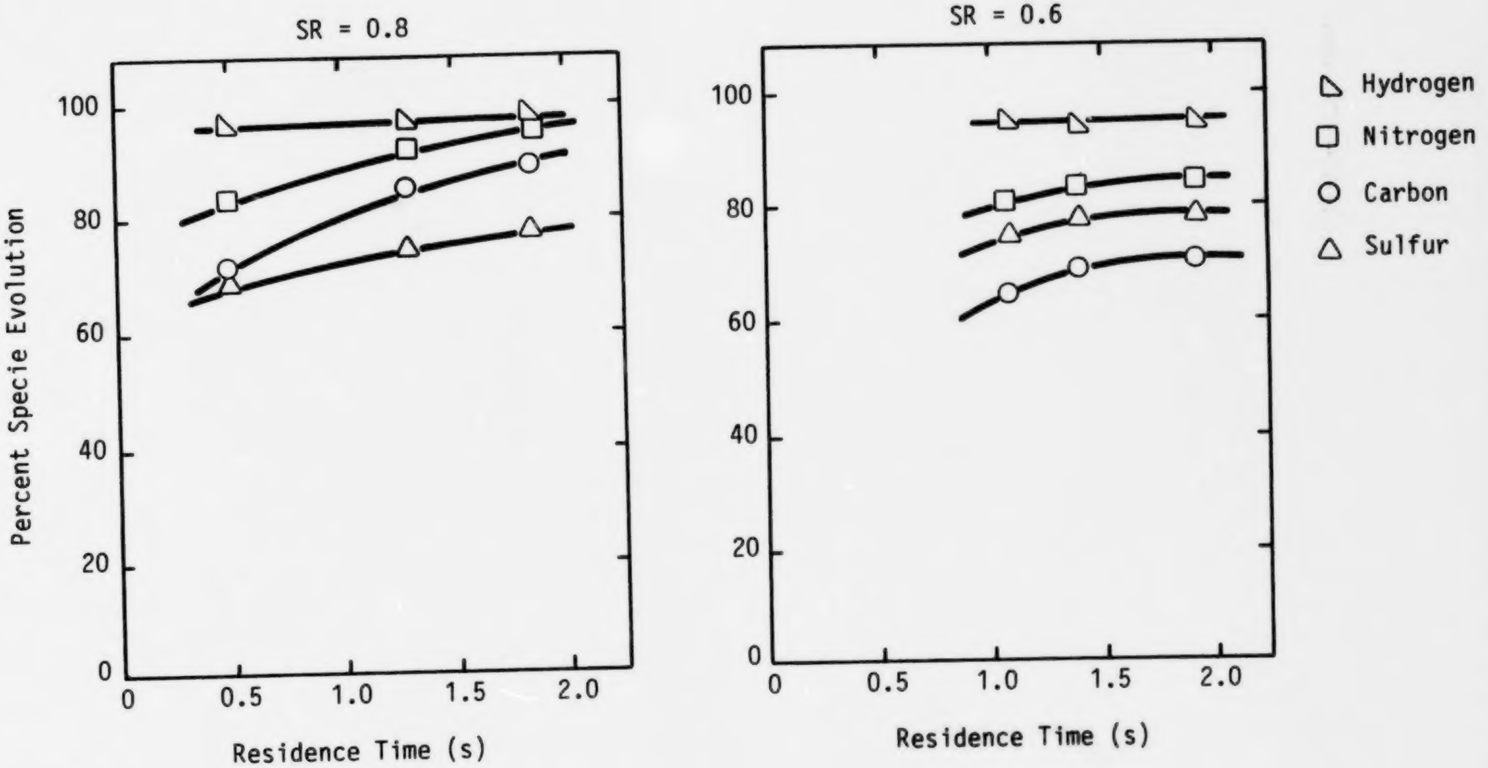


Figure 6-13. Species evolution from Illinois coal in the CTT at 17.6 kW (60,000 Btu/hr).

combustion of coal on precombustor walls or by aerodynamically suspended combustion are potential requirements for effective precombustor designs.

For the case of higher stoichiometry (i.e., more fuel-lean), the H_2S and COS levels were reduced while the SO_2 concentration rose down the length of the reactor. From these results alone it is difficult to determine how the sulfur evolved from the coal, particularly considering the incomplete char burnout. Figure 6-14 shows, along with measured gas phase sulfur speciation data, the calculated equilibrium distribution of sulfur species at each sample point. The equilibrium values were calculated based on the local gas phase stoichiometry and measured temperature. At each sample point, the local stoichiometry is higher than the overall calculated stoichiometry due to slow carbon utilization.

The results show that the excess O_2 conditions found early in the coal flame thermodynamically favor the formation of SO_2. The fact that the measured sulfur species were relatively low in SO_2 and high in H_2S and COS in the early portion of the flame indicates that a significant amount of the sulfur must have evolved in the form of H_2S and/or COS. In other words, if the sulfur evolved as SO_2, equilibrium considerations would indicate that no H_2S or COS should be present early in the coal flame. The measured sulfur speciation began to shift towards the equilibrium levels by the end of the reaction zone. The direct evolution of reduced sulfur species favors fast reaction with calcium based sorbents. However, slowly evolving carbon can cause higher local stoichiometries which favor higher SO_2 concentrations and lower sulfur capture by the sorbent in the early portion of the reactor.

Figure 6-12 presents the capture data as a function of residence time. Capture levels rose to about 80 percent of the ultimate capture level within approximately 0.4 seconds. Just as was found with the ITR data, the initial reactor conditions in which the sorbent is injected into appear to be crucial to the ultimate capture achieved. This suggests that in a practical precombustor system, the sorbent be separated from the incoming fuel. This would allow the sulfur to evolve and speciate into desirable sulfur species before the sorbent is injected and experiences its peak reactivity.

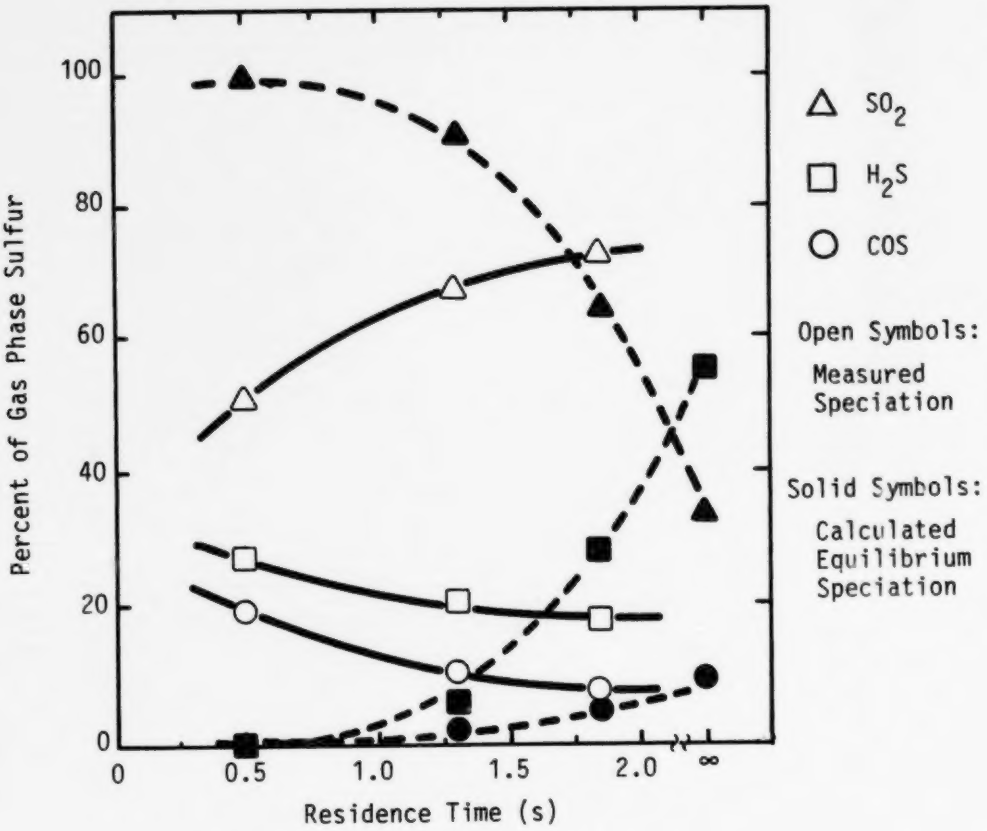


Figure 6-14. Comparison of measured gas phase sulfur speciation from an SR = 0.8 Illinois coal flame to equilibrium speciations calculated at conditions which correspond to the local measured stoichiometry and temperature.

Solid sample analysis for calcium utilization was calculated based on the assumption that the sulfur evolved from the coal at the same rate when sorbent was present as when it was not present. The solid sample capture results corresponded well with gas phase capture data (see Figure 6-12) indicating once more the validity of the sampling techniques and supporting the capture levels.

6.2.2 Load Effects

Two reactor loads were tested to help determine the sensitivity of the process to thermal environment. The high load case of 23.4 kW (80,000 Btu/hr) gave a slightly higher sorbent injection temperature (see Figure 5-6) and a higher average reactor temperature than the 17.6 kW (60,000 Btu/hr) case. In addition, at the same stoichiometry the high load case produced a 33 percent higher exhaust flowrate. This caused a corresponding reduction in reactor residence time. As Figure 6-15 shows, these changes in reactor conditions had little impact on reaction rates or ultimate capture. The rate and extent of species evolution and the speciation of evolved sulfur compounds was similar for both cases as shown in Figures 6-16 and 6-17, respectively. These results indicate that the process is relatively insensitive to furnace load conditions; however, the CTT facility did not show a great change in thermal environment as load was changed. The data obtained at these two loads is more a confirmation of the repeatability of the results than a test of the impact of thermal environment.

6.2.3 Impact of Sorbent Type and Feed Rate

Both Linwood AH and Vicron 45-3 were tested at the 23.4 kW (80,000 Btu/hr) load, SR = 0.6 furnace condition. Figure 6-18 presents the percent reduction of total sulfur input to the system as a function of Ca/S molar ratio. The Ca/S molar ratio is a way of expressing the changing sorbent feedrate relative to the amount of sulfur present. As expected from the ITR results and results from fuel-lean sulfation tests, the capture ability of Linwood hydrate was substantially higher than Vicron carbonate (a factor of 2 to 3 times higher).

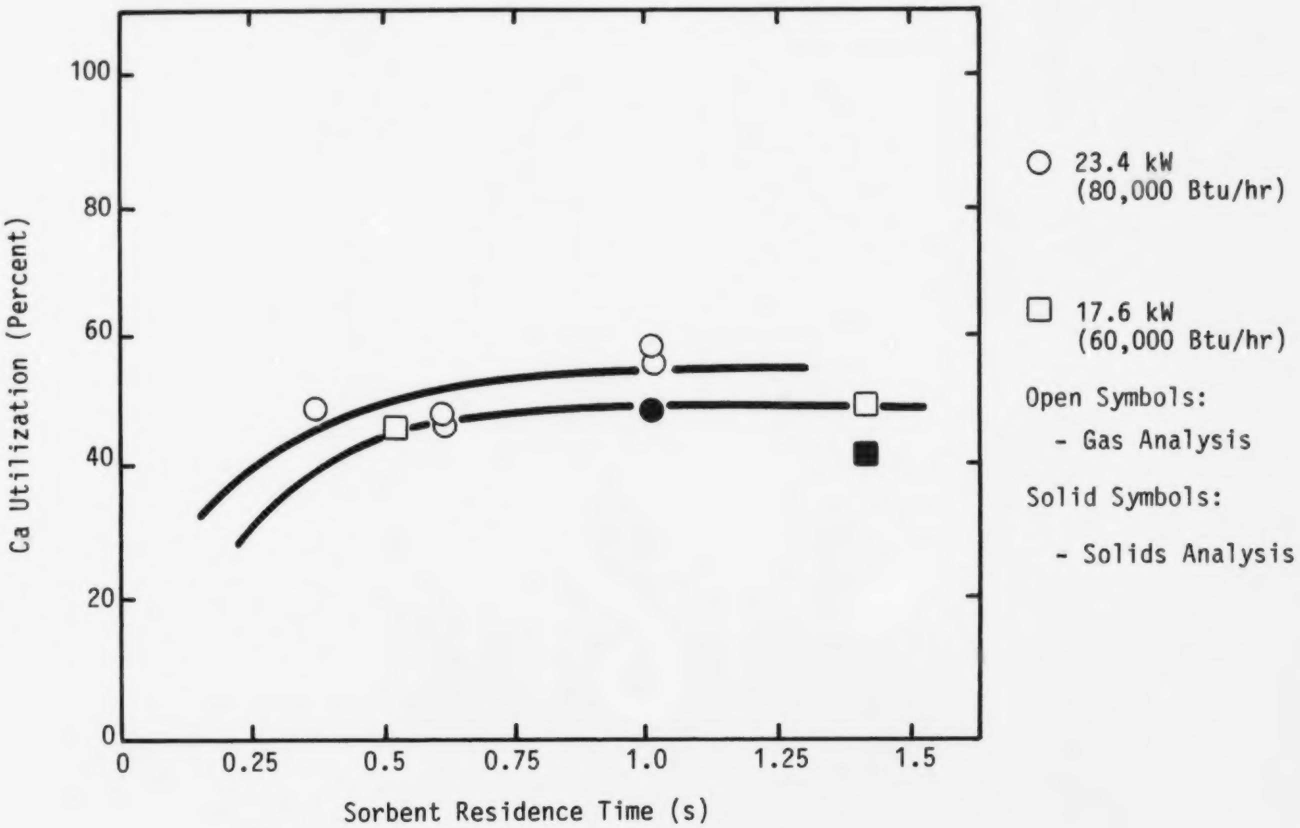


Figure 6-15. Calcium utilization in the CTT firing Illinois coal at SR = 0.6 injecting Linwood atmospheric hydrate at about Ca/S = 1.0.

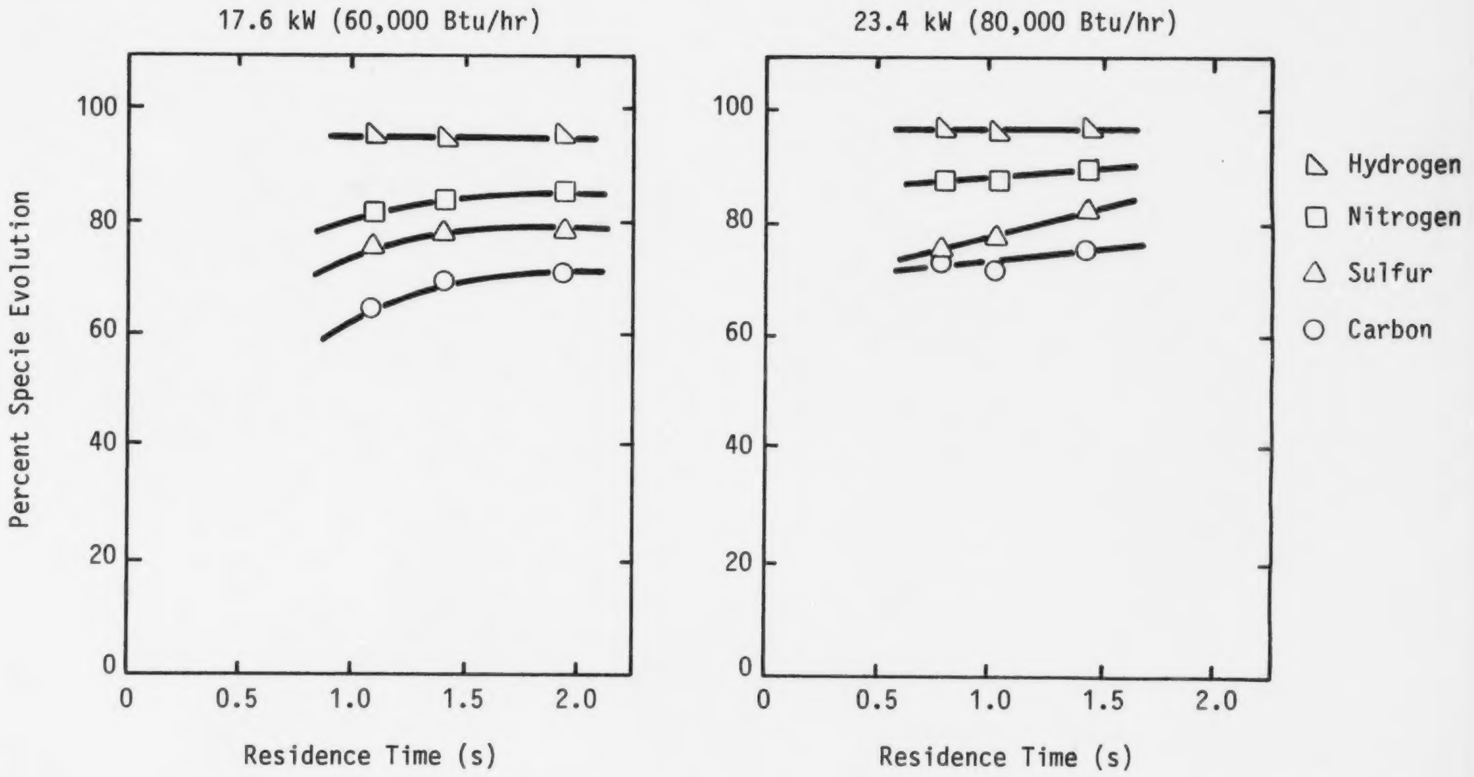


Figure 6-16. Species evolution from Illinois coal in the CTT at SR = 0.6.

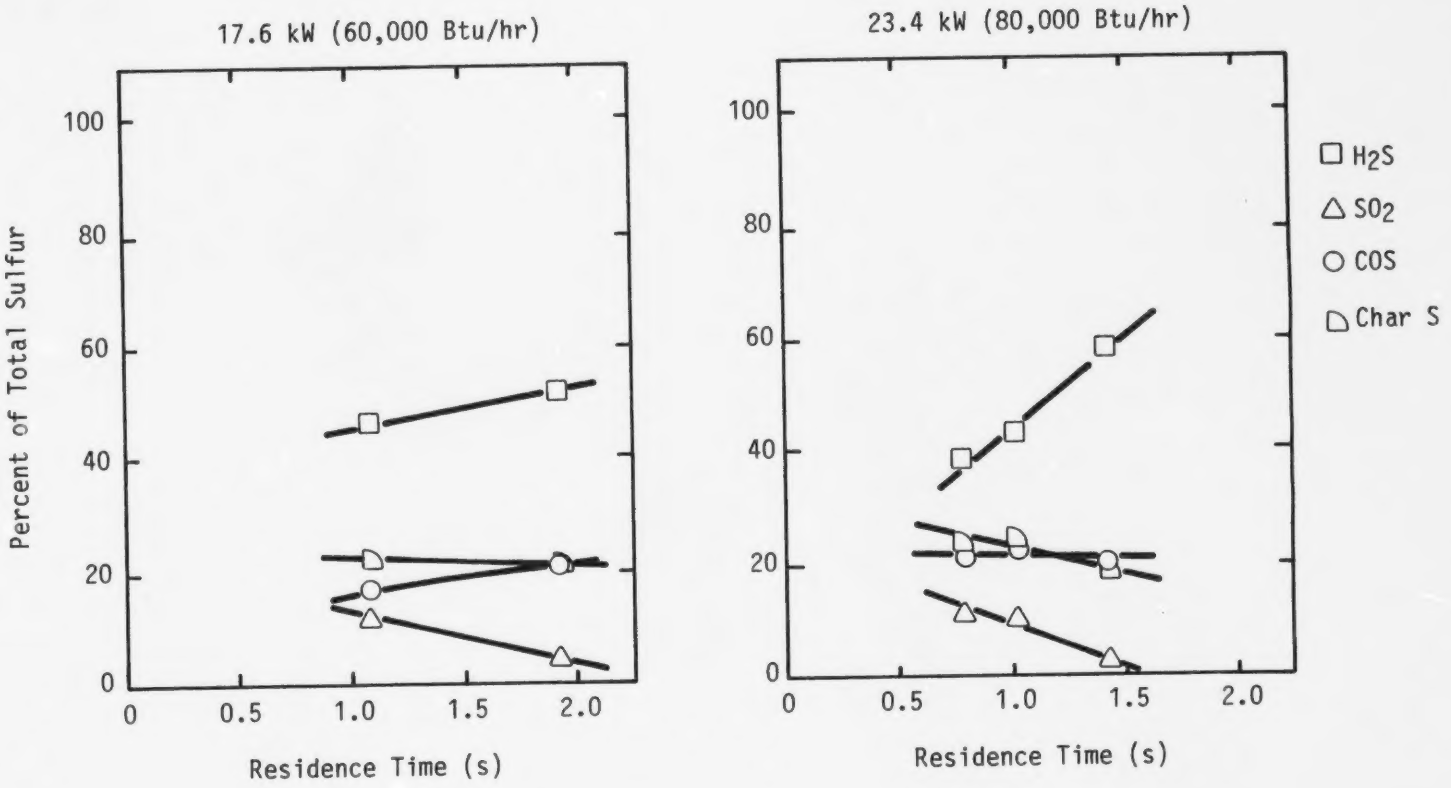


Figure 6-17. Sulfur speciation in the CTT firing Illinois coal at SR = 0.6.

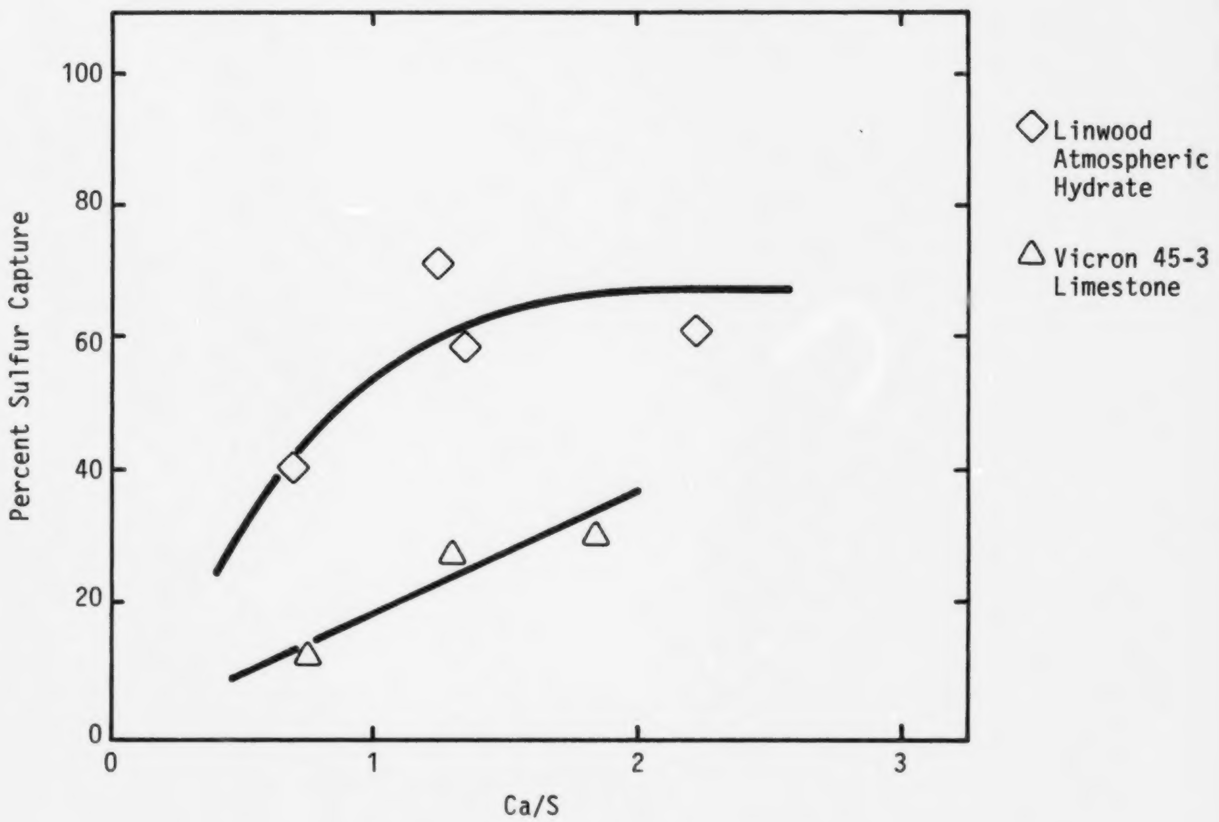


Figure 6-18. Capture of total sulfur in the CTT by the injection of sorbents when firing Illinois coal at 23.4 kW (80,000 Btu/hr), SR = 0.6. Both sulfur capture and Ca/S calculated based on the total input sulfur.

One reason that the capture level appears to begin to plateau near 55 to 60 percent capture for the Linwood case is that a substantial portion of the sulfur is not available for capture. Around 25 percent of the sulfur is still bound to the char while approximately 10 percent of the gas phase sulfur is in the form of SO_2 (see Figure 6-17). When the sulfur capture is calculated based only on the gas phase sulfur (along with the determination of Ca/S), the capture levels are substantially higher, as shown in Figure 6-19. This representation demonstrates the importance of evolving as much of the sulfur from the coal char as possible to make it available to the sorbent for capture. Carbon burnout and sulfur evolution would be expected to be near 100 percent in a practical precombustor system.

6.2.4 Effect of Injection Temperature

An important factor in application of this technology is defining a range of operating temperatures which will accommodate the various process requirements in an acceptable fashion. For instance, high slag fluidity and carbon burnout in practical precombustor systems require very high temperatures (up to 1400°C (2550°F)) while sorbent tends to become less reactive above about 1200°C (2192°F) due to thermal sintering. With the reactor at 23.4 kW (80,000 Btu/hr) and SR = 0.6, the injector location was moved to produce different injection temperatures. Figure 6-20 shows that the calcium utilization is optimum below about 1300°C (2372°F) and is still quite high at a temperature of about 1420°C (2588°F). The optimum injection temperature corresponds well to results on the ITR facility considering that the optimum may be shifted slightly to higher temperatures on the CTT since the sorbent is injected with cool carrier gas. The heating rate of the sorbent injection stream in conjunction with the furnace quench rate produces a lower peak sorbent particle temperature than the measured injection temperature. This phenomena is not found on the ITR since the reactor is isothermal.

All of the results presented so far have shown that entrained flow reactions between reactive CaO and H_2S or COS can be fast (less than 400 ms) and substantial (up to 60 percent calcium utilization for an atmospheric

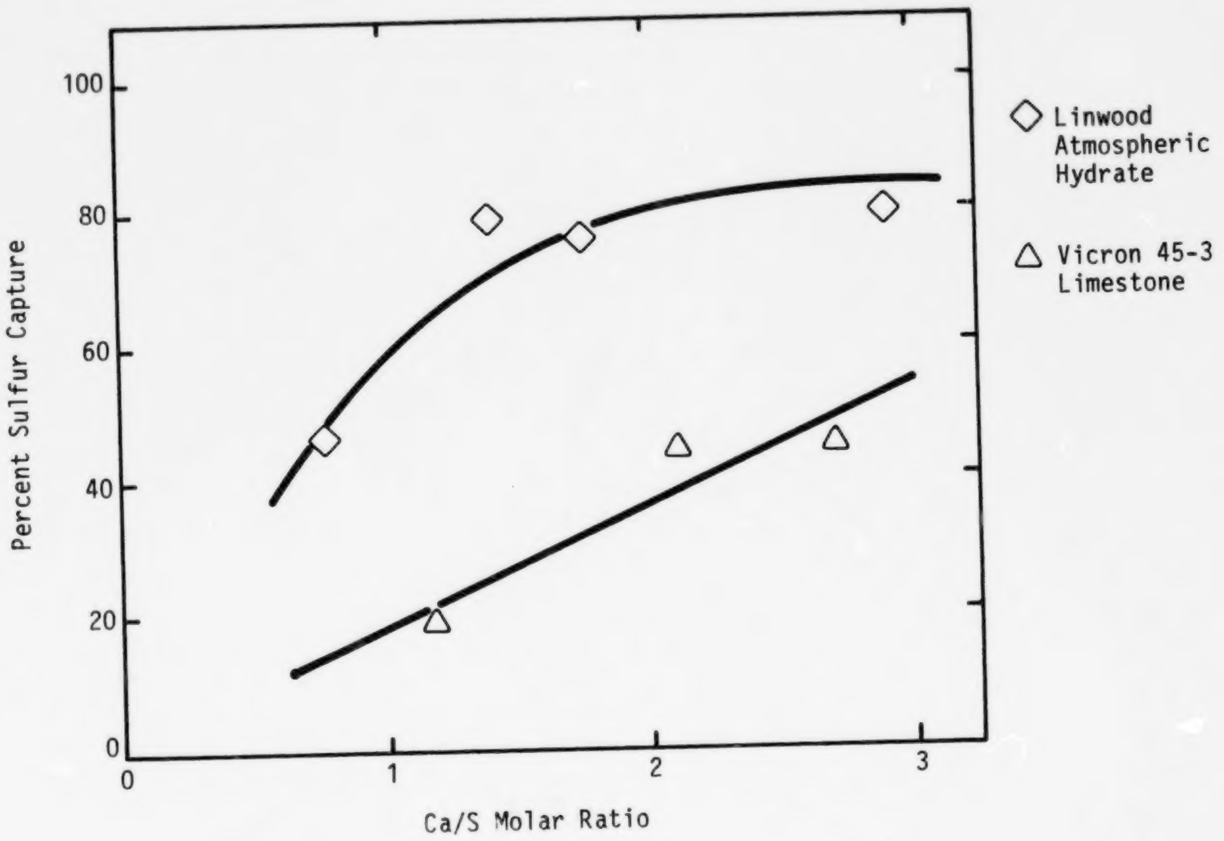


Figure 6-19. Capture of gas phase sulfur in the CTT by the injection of sorbents when firing Illinois coal at 23.4 kW (80,000 Btu/hr), SR = 0.6. Both sulfur capture and Ca/S calculated based on the measured gas phase sulfur.

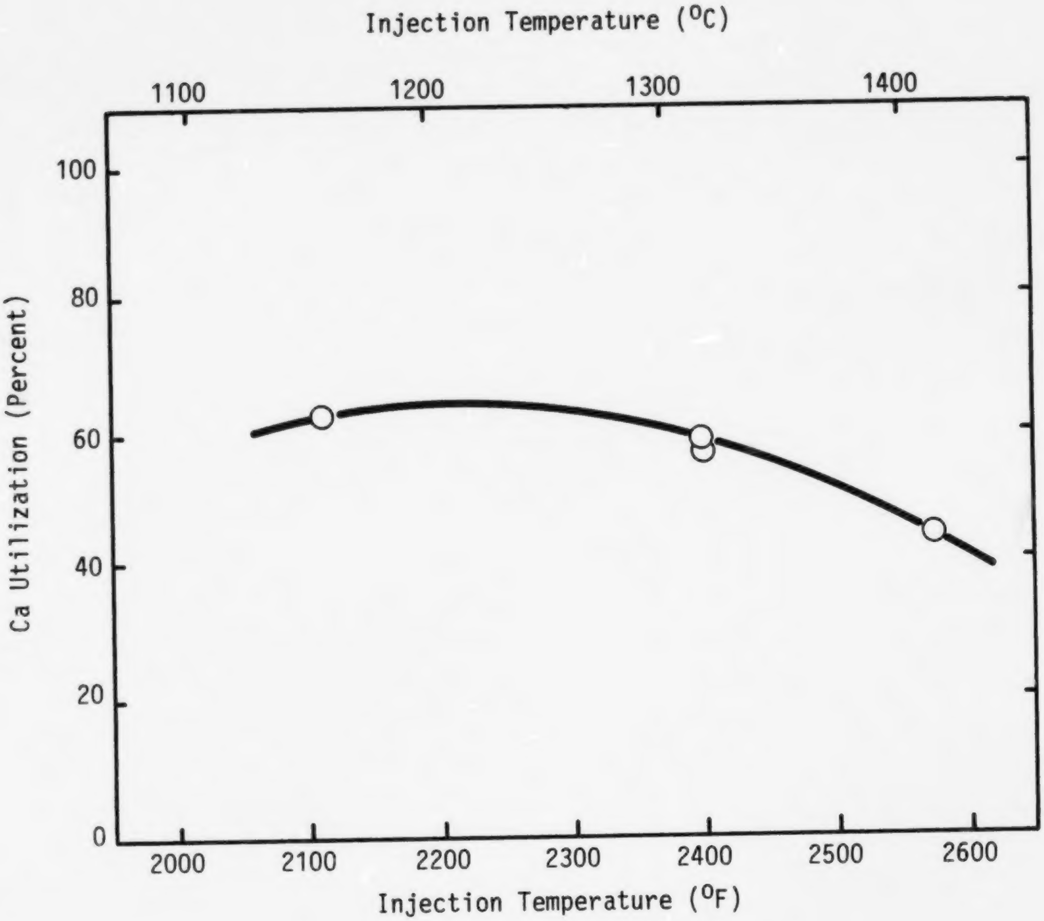


Figure 6-20. Calcium utilization as a function of Linwood atmospheric hydrate injection temperature in the CTT firing Illinois coal at 23.4 kW (80,000 Btu/hr), SR = 0.6.

hydrate). It has also been shown (see Section 3-3) that CaS is not stable when passing through oxidizing flame zones so that the reacted sorbent must be removed from the fuel-rich zone of a precombustor. This would most easily be done by drainage through the molten slag drain. The mixture of CaS with molten coal ash presents a new set of critical issues:

- Is sulfur stable in molten mixtures of CaS and coal ash?
- If not stable, what is the rate of sulfur regeneration?
- How does the presence of increased calcium effect slag fluidity?
- Are there additives which can enhance the fluidity or sulfur solubility of the slag?

These important issues are addressed in the following section.

7.0 SLAG SULFUR CHEMISTRY RESULTS

In order to determine the impact of calcium-based sorbents and other additives on slag sulfur solubility and fluidity, mixtures of Illinois coal ash and additives were placed in the high temperature oven described in Section 5.3 and exposed to a thermal and gaseous environment that simulated a fuel-rich slagging precombustor.

7.1 Sulfur Solubility and Equilibrium

The equilibrium level of sulfur in a liquid slag when exposed to a fuel-rich, sulfur bearing gas stream can be characterized by the "sulfur capacity", defined by Fincham and Richardson (1954) as:

$$C_s = (\text{wt \% S}) \, (P_{O_2}/P_{S_2})^{1/2}$$

where P_{O_2} and P_{S_2} are the partial pressures of oxygen and sulfur, respectively. The value of C_s can be determined by equilibrating a slag at a known temperature and interfacial gas composition. The amount of absorbed (or released) sulfur can be determined by measure of sulfur concentration in the slag before and after a test. Illinois coal ash and mixtures of CaO/coal ash and Fe_2O_3/coal ash were tested at 1200°C (2192°F) and 1400°C (2552°F) in gas environments that simulated the exhaust gases of an Illinois coal flame at SR = 0.5. The synthetic exhaust gas mixing system was described in Section 5.3 and its inlet composition is presented in Table 7-1.

A sample exposure time of at least 12 hours was established as the minimum testing time to assure an equilibrium level of sulfur in the slag sample. Figure 7-1 shows an example of the rate of sulfur gain for a mixture of CaO and Illinois coal ash (Ca/S = 2.0) at 1400°C. The rate of sulfur capture was extremely slow for three reasons: 1) the CaO was well mixed with the coal ash so that a majority of the sorbent was not in ready contact with the sulfur-laden gas stream, 2) the CaO used in these tests was much less reactive than the freshly calcined CaO derived from injection of $Ca(OH)_2$ or $CaCO_3$ as in the entrained flow studies, and 3) the heating rate was probably

TABLE 7-1. HTO FEED GAS COMPOSITIONS

Stoichiometric Ratio	Gas Composition, Vol. Percent			
	N_2	CO	CO_2	H_2S
0.5	68.25	26.35	4.90	0.50
0.7	74.96	13.35	11.19	0.50

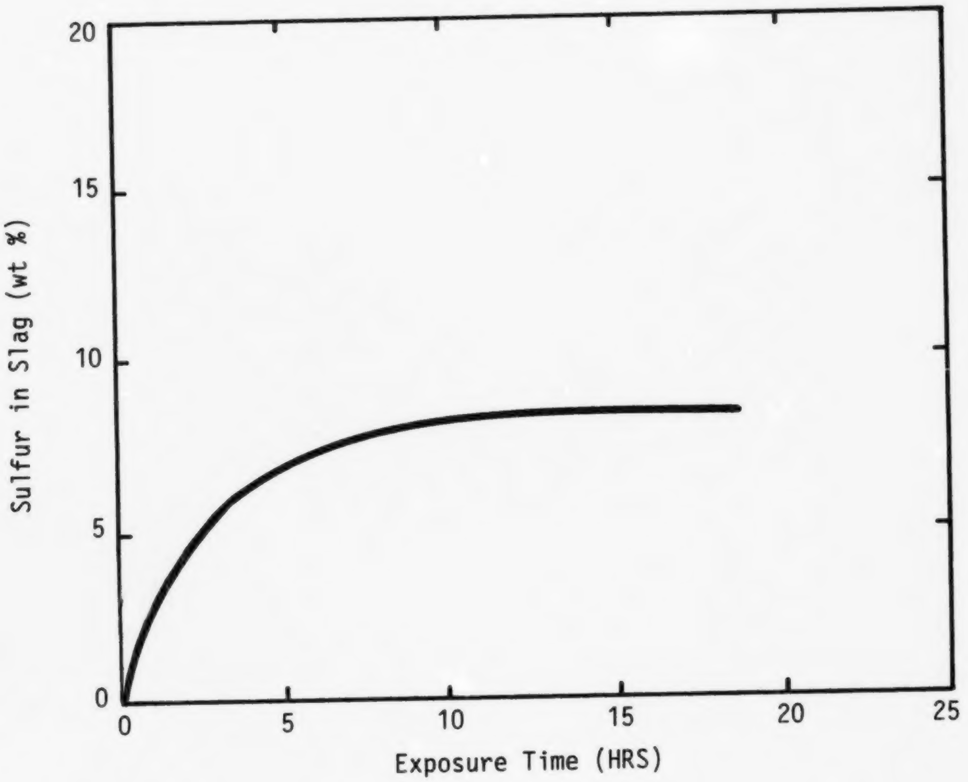


Figure 7-1. Slag exposure time requirements for Illinois coal ash/CaO slag corresponding to a Ca/S = 2 at 1400°C, SR = 0.5.

faster than the sulfur uptake rate, so that the sulfur capture mechanism was predominantly between gas phase sulfur and molten slag rather than reaction directly with CaO particles.

Values of log C_s are presented in Figure 7-2 versus temperature. Data by DeYoung (1984) and Fincham and Richardson (1954) have been included to show the consistency of EER results with the literature and to compare to reported trends. Note that mixtures of Fe_2O_3 and coal ash gave results similar to the literature, giving validity to the testing and analysis techniques used. Figure 7-3 presents log C_s as a function of molar basicity for iron silicate mixtures to again show that the EER experimental system produces trends similar to what has been presented in the literature.

High sulfur capacities were obtained with CaO/coal ash mixtures of high molar basicity (defined by the ratio of total moles of base constituents to acid constituents). However, the mixture fluidity was reduced at high calcium contents. The mixtures of CaO and coal ash were established based on what would be expected when burning Illinois coal at Ca/S molar ratios of 0.5, 1.0 and 2.0. Therefore, the most effective slag mixtures in terms of sulfur retention are too refractory for slag drainage out of a practical precombustor system.

The relationship between the sulfur capacity and temperature varied with molar basicity, increasing with higher temperature for high molar basicity but decreasing with higher temperature at low molar basicity. There is no clear explanation for this behavior at this time.

By combining the equilibrium sulfur capacity of the slag mixture with expected gas phase equilibrium composition and a mass balance on the amount of slag that accumulates, it was possible to predict the equilibrium amount of sulfur captured by the slag. Figure 7-4 presents families of curves that correspond to varying slag sulfur capacities and amounts of accumulated slag (in grams of slag per gram of injected coal). In other words, the curves identify the required sulfur capacity to get a desired sulfur removal percentage for a given ash-plus-additive slag mass.

■ Iron Silicate, molar basicity = 1.65, Fincham & Richardson (1954).

● Iron Silicate, molar basicity = 3.03, DeYoung (1984).

☗ Fe_2O_3/Coal Ash (Fe/S = 4.4), molar basicity = 3.01, EER.

✚ Fe_2O_3/Coal Ash (Fe/S = 4.0), molar basicity = 2.75, EER.

◣ Fe_2O_3/Coal Ash (Fe/S = 2.55 + 15.1% MgO), molar basicity = 3.08, EER.

△ CaO/Coal Ash (Ca/S = 2), molar basicity = 2.77, EER.

◇ CaO/Coal Ash (Ca/S = 1), molar basicity = 1.48, EER.

⬢ CaO/Coal Ash (Ca/S = 0.5), molar basicity = 0.83, EER.

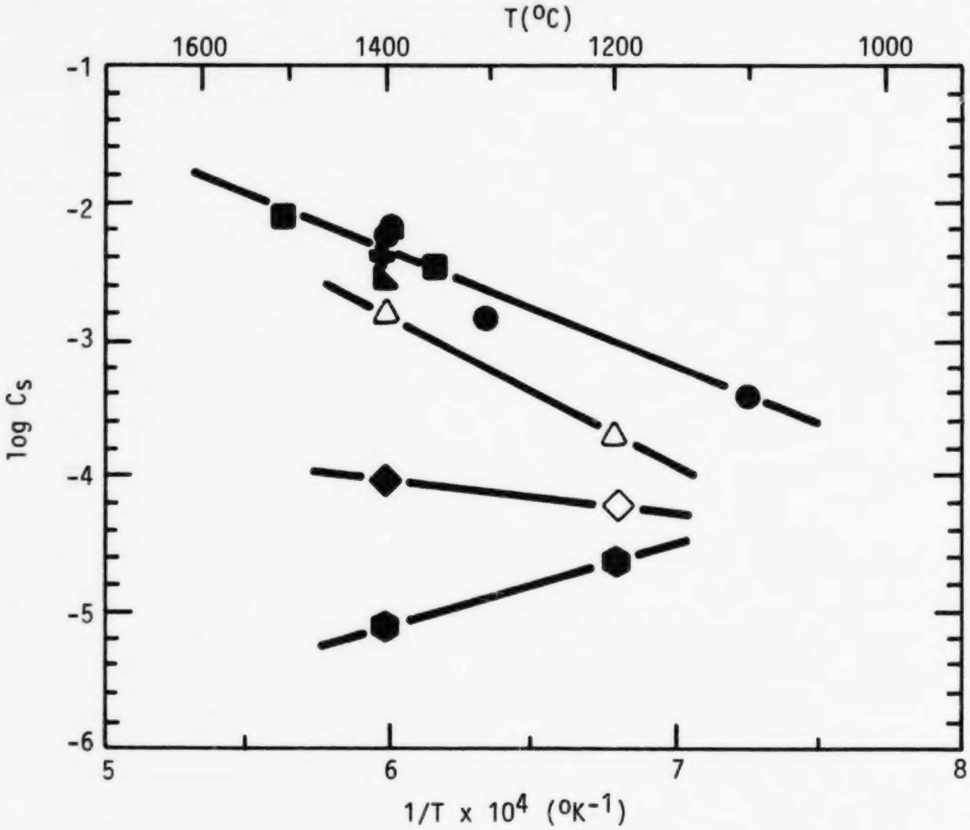


Figure 7-2. Influence of temperature and molar basicity on sulfur capacity for several slag mixtures (solid symbols - melted, open symbols - not melted).

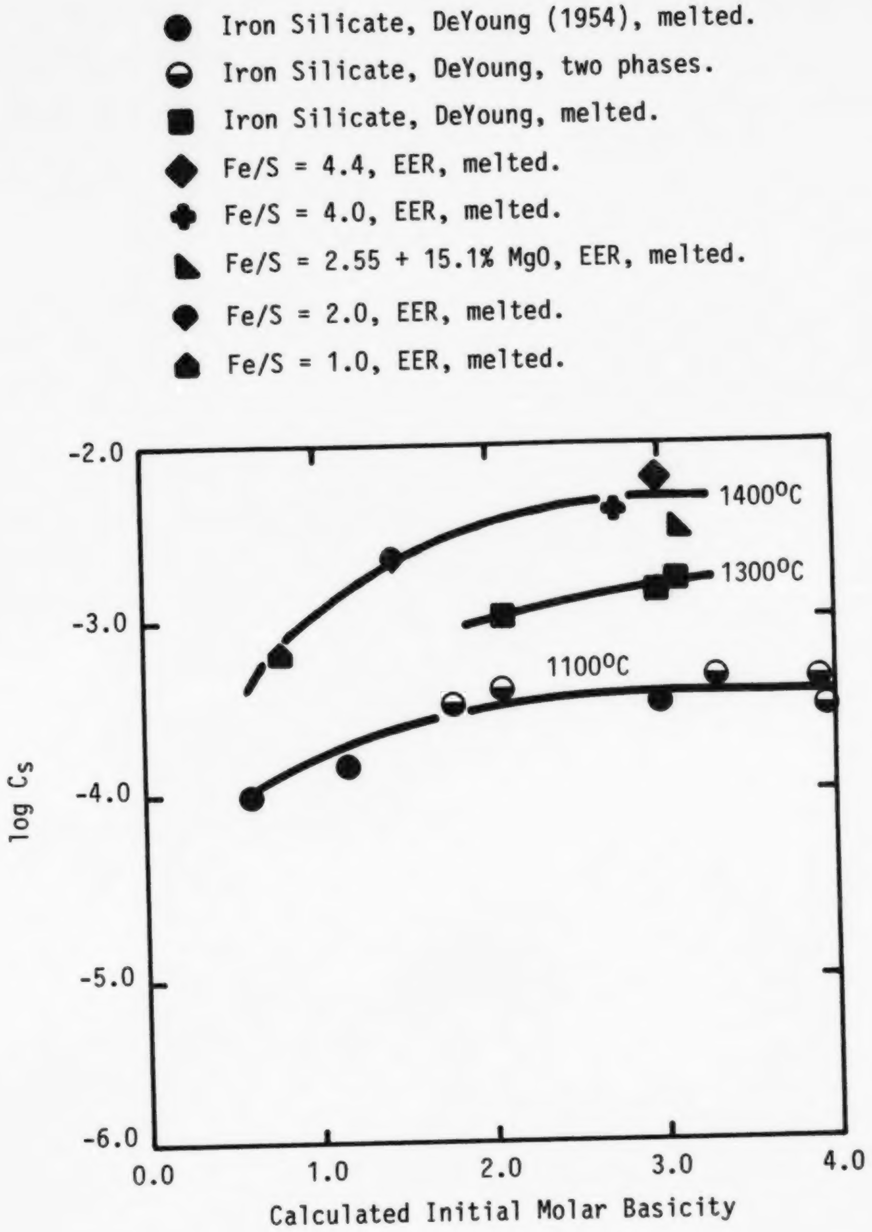


Figure 7-3. Sulfur capacity for iron silicate melts at various initial slag molar basicities.

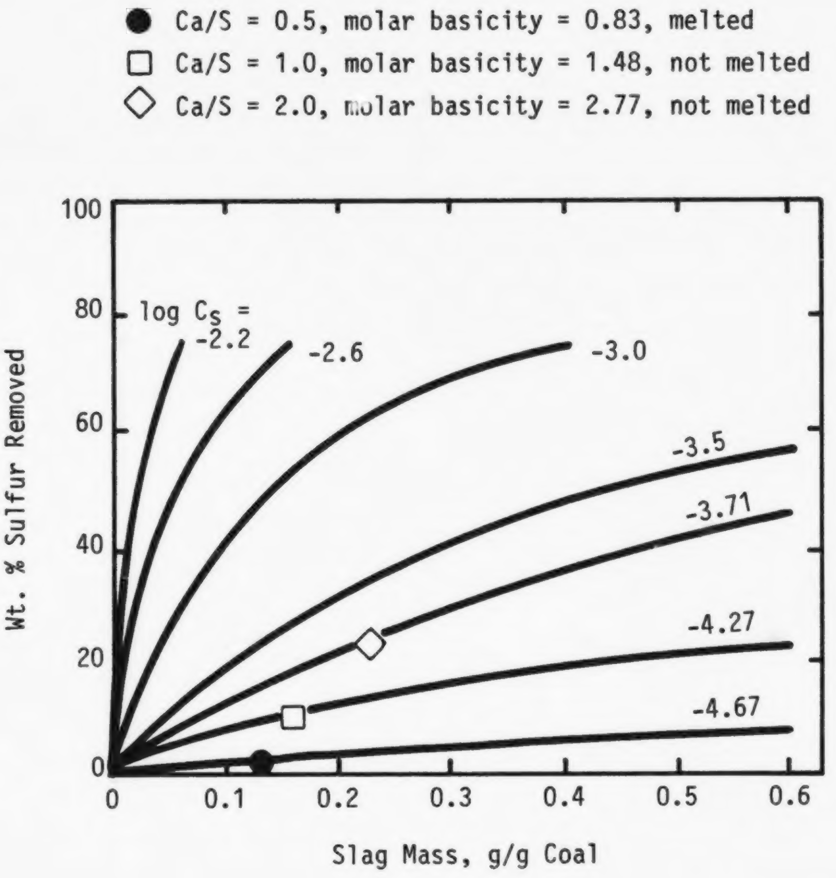


Figure 7-4. Equilibrium sulfur removal by slag for SR=0.5, T=1200°C, and an Illinois coal with 3.97% sulfur.

The data points on Figures 7-4 and 7-5 correspond to Illinois coal ash combined with different amounts of added CaO or Fe_2O_3. The greater the amount of additives, the greater the relative slag mass. For this coal, no additives correspond to the ash content of the coal - 9.5 percent or 0.095 g slag/g coal. CaO addition of 23.5, 39.8 and 57.78 percent by weight (totaling 26.89, 42.14 and 58.81 percent CaO in the slag mixture when considering the CaO originally present in the ash) corresponds to burning the coal at Ca/S molar ratios of 0.5, 1.0 and 2.0, respectively.

At best, the equilibrium level of sulfur held in the slag corresponds to 25 percent of the total input sulfur for CaO/coal ash mixtures. Note, also that at a temperature of 1400°C (2252°F) the slag mixtures with higher CaO content were not melted. Even without considering the kinetic limitations of a slag sulfur capture process, large amounts of sulfur were not stable in the slag and the required temperatures for complete slag fluidity were higher than available under typical combustor operating conditions.

At first look, the addition of Fe_2O_3 as an additive looks promising. A large amount of sulfur was captured and the slag remained molten at 1400°C. However, there is no fast kinetic mechanism for getting sulfur into the slag in conventional precombustor designs. Also, an excessive amount of Fe_2O_3 additive was required (a ratio of Fe/S = 4 or a weight percent of 82.98 percent corresponds to an addition of 3.85 times the total ash content of the coal).

Researchers at Alcoa (Stewart et al., 1984) have reported the difficulties of capturing sulfur in a fuel-rich, slagging precombustor by forming an iron-based slag layer. They reported sulfur capture levels below 15 percent when relying on a mixture of iron ore and sand as the slag additive (at a level of approximately 25 percent of the coal feed) while burning out only 68-87 percent of the carbon.

The preceding results demonstrate that using the slag layer as a mechanism for sulfur capture and retention is not a promising scheme since equilibrium solubility is low. Also, the problem of slag fluidity upon

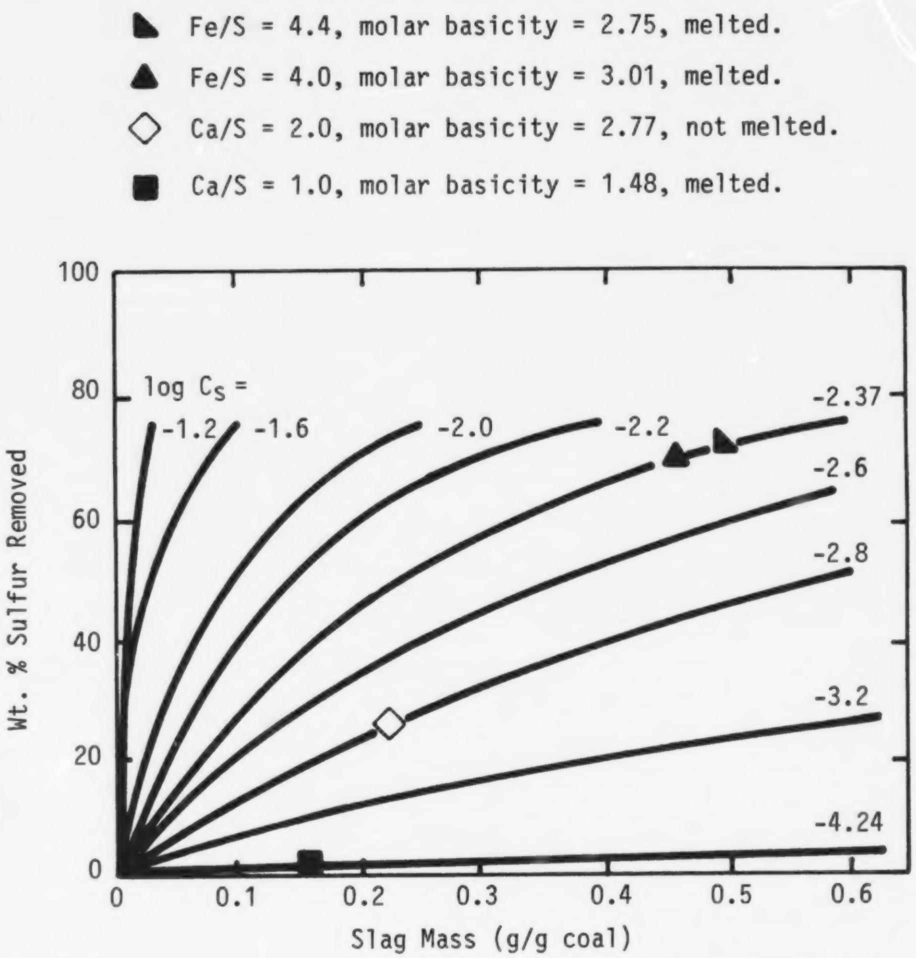


Figure 7-5. Equilibrium sulfur removal by slag for SR=0.5, T=1400°C, and an Illinois coal with 3.97% sulfur.

mixture with large amounts of calcium compounds has been identified as a practical problem in slagging precombustors. Since the entrained flow reaction of CaO and H_2S/COS was found to be a promising sulfur capture mechanism (see Section 6.0), the following subsections address issues that would make the entrained flow process viable under slagging conditions, such as: 1) means of improving slag fluidity for operation at lower temperature or higher calcium contents, and 2) determination of the rate in which slag desulfurization takes place when CaS comes into contact with molten slag.

7.2 Impact of Slag Fluxing Additives

The effect of CaO on the fluid temperature of Illinois coal ash is shown graphically in Figure 7-6. The fluid temperatures were determined by the ASTM ash fusion procedure. Small amounts of added CaO, up to levels corresponding to coal firing at a molar ratio of Ca/S = 1, produced melting temperatures below that of the raw ash. Beyond Ca/S = 1 the melting temperature rose to higher and higher levels. However, Illinois coal is a particularly high sulfur coal so that at Ca/S = 1 a relatively large amount of calcium was added. Other coal slags may withstand much higher Ca/S levels before reaching unacceptable fluid temperatures.

Four additives were investigated for their influence on CaO/coal ash slags: Fe_2O_3, CaF_2, B_2O_3 and P_2O_5. These additives were selected based on their use in the glass and steel industries and by review of ternary phase diagrams (Levin et al., 1979). For each additive, both the fluid temperature and the sulfur capacity under reducing conditions were measured. Figure 7-7 and Table 7-2 present the results of these additive tests. The most effective additive for reducing the slag fluid temperature for both Ca/S = 1 and Ca/S = 2 mixtures was boric oxide (B_2O_3), causing a drop in fluid temperature of about 150°C (270°F) down to a temperature of 1055°C (1930°F) by an addition of 10 percent by weight to a Ca/S = 1 slag mixture. Iron oxide (Fe_2O_3) was the most effective additive in increasing the sulfur capacity, changing log C_s from -3.95 to -3.83 when a 10 percent by weight addition was made to a Ca/S = 1 slag mixture at 1400°C (2552°F). However,

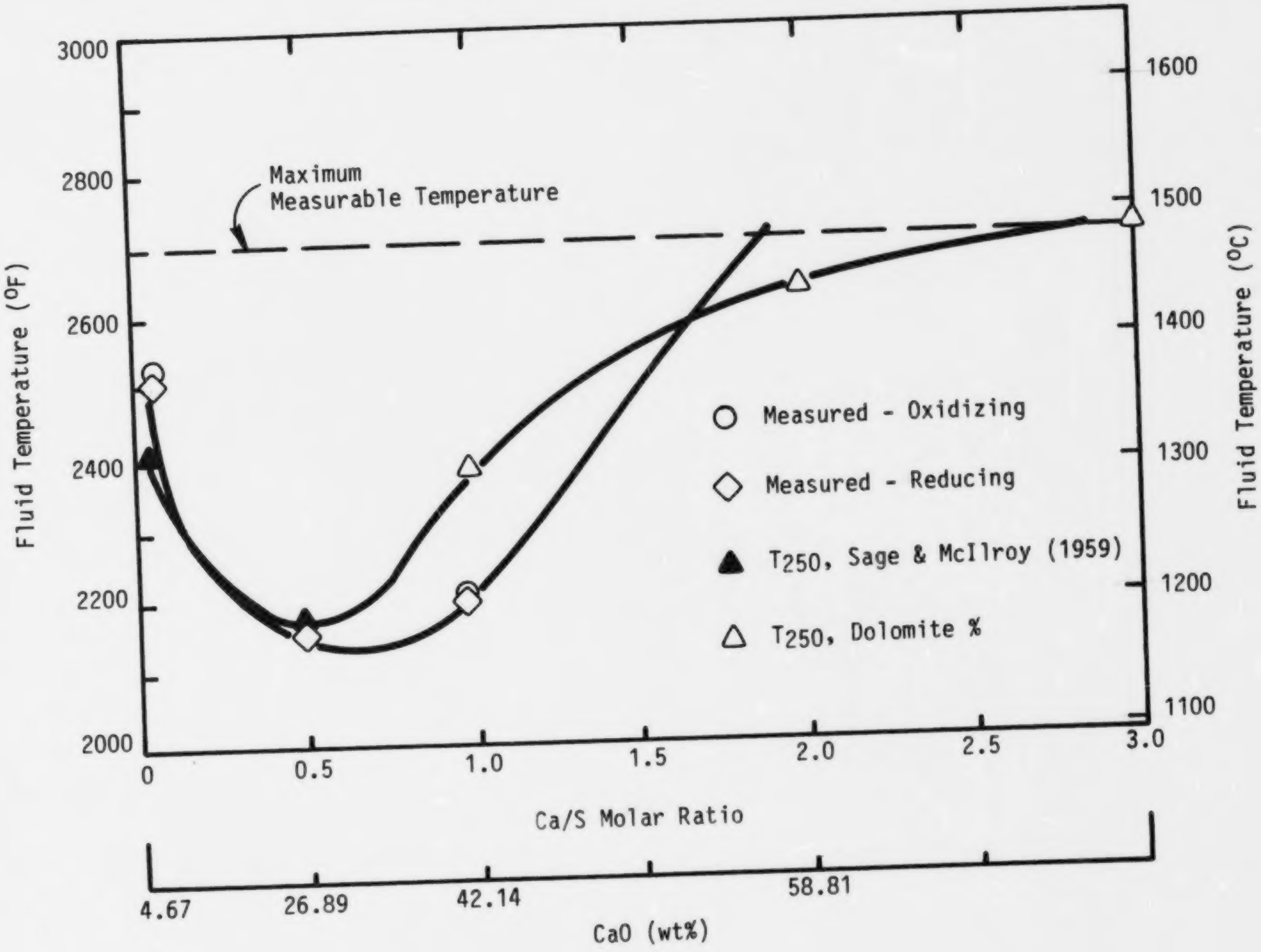


Figure 7-6. Fluid and T_{250} temperatures for Illinois coal ash/CaO mixtures.

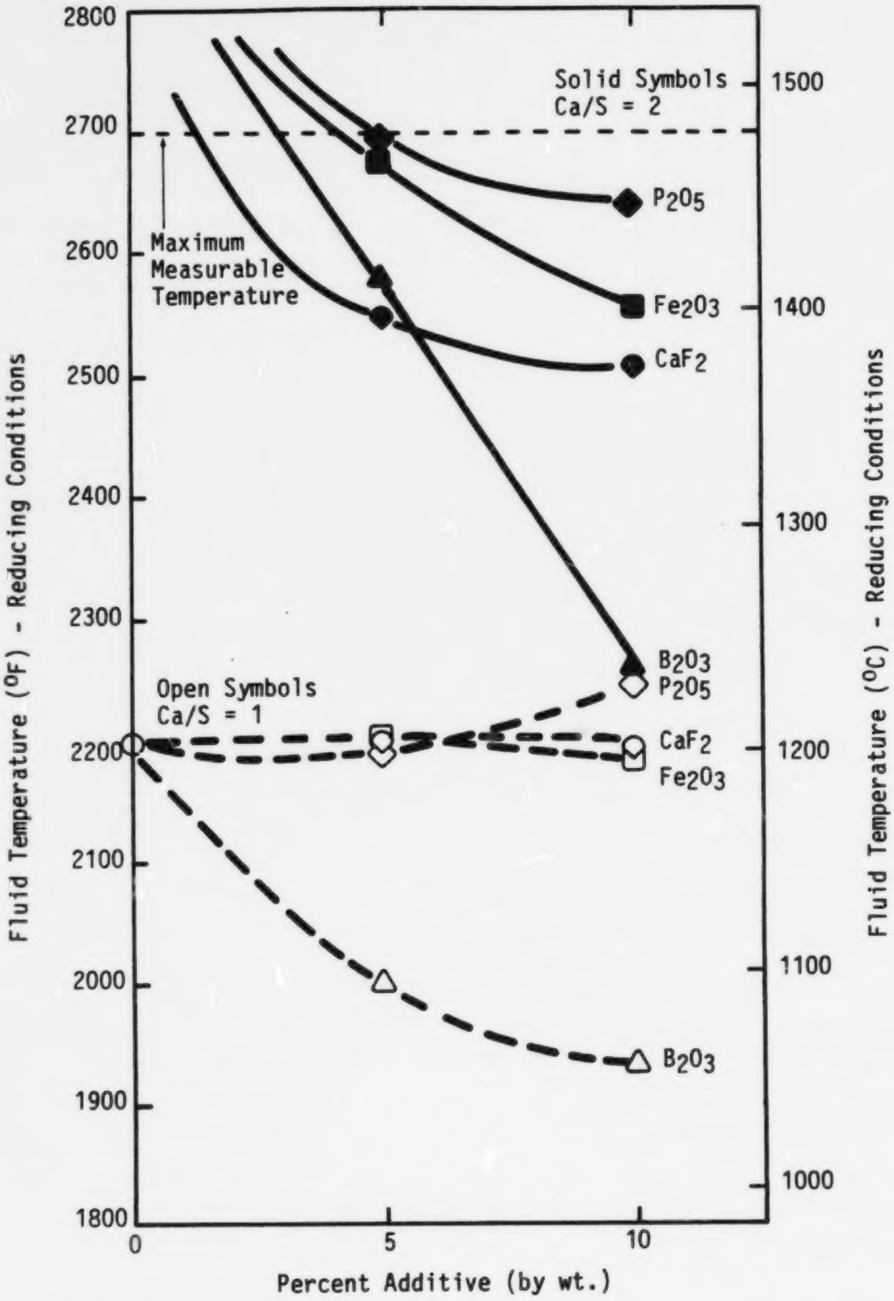


Figure 7-7. Influence of fluxing additives on the reducing fluid temperature of Illinois coal ash and CaO mixtures (open symbols correspond to Ca/S = 1 mixtures while solid symbols represent Ca/S = 2 mixtures).

TABLE 7-2. INFLUENCE OF SLAG ADDITIVES ON SULFUR CAPACITY
Ca/S = 1; log C_s determined at 1400°C, SR = 0.5

	Additives				
	None	Fe_2O_3	CaF_2	B_2O_3	P_2O_5
log C_s (5% Additives by Wt.)	-3.95	-3.89	-3.81	-4.09	-4.09
log C_s (10% Additives by Wt.)	-3.95	-3.83	-4.16	-4.32	-4.26

this rise in C_s of 32 percent will not make a large difference in the total sulfur solubility of the slag.

7.3 Slag Desulfurization Rates

So far, the most promising scenario for reducing sulfur emissions from slagging precombustors is as follows: calcium-based sorbent is injected into the precombustor to capture sulfur through entrained flow formation of CaS; deposition of the CaS onto the molten slag covered walls; and rapid slag rejection before the CaS can dissolve into the slag, releasing the sulfur back into the gas phase. The issue that had not been investigated was the rate at which the sulfur was regenerated.

The desulfurization rate of slags that hold a super-equilibrium amount of sulfur were tested by replacing the CaO in previously tested slag mixtures with CaS. The slag mixtures were then exposed to a 1400°C environment for 12, 30 and 60 minutes. A blended gas stream which simulated an equilibrium coal flame effluent stream at SR = 0.5 was passed continuously over the samples, just as was done in establishing the slag sulfur capacities reported in Section 7.1. Figure 7-8 shows that the rate of desulfurization varies for different slag mixtures. The desulfurization process was faster for cases in which the CaS and ash mixtures were better mixed and for slag mixtures having lower sulfur capacities. Notice that pure CaS was stable under these fuel-rich, high temperature conditions.

Figure 7-9 shows the impact of fluxing additives on the desulfurization of CaS/coal ash mixtures. An addition of 10 percent by weight of Fe_2O_3 had little impact on a Ca/S = 1 slag mixture, while 10 percent additions of B_2O_3 to both Ca/S = 1 and 2 slag mixtures caused significant increases in the desulfurization rate. It is apparent that mixtures with lower fluid temperatures have higher rates of desulfurization.

The data presented in Figure 7-8 can be used to determine a rate constant according to the desulfurization rate expression developed by Turkdogan and Pearce (1963):

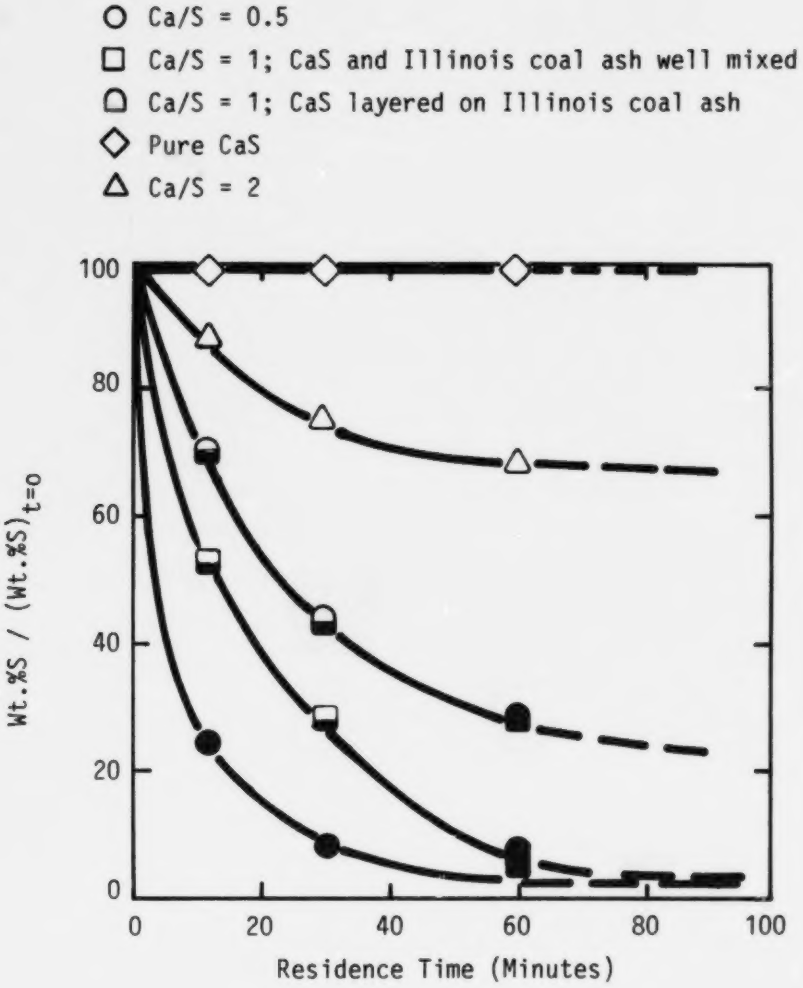


Figure 7-8. Desulfurization of CaS and Illinois coal ash slag mixtures, showing the influence of calcium content and mixedness (open symbols represent completely unmelted samples, solid symbols correspond to completely melted samples).

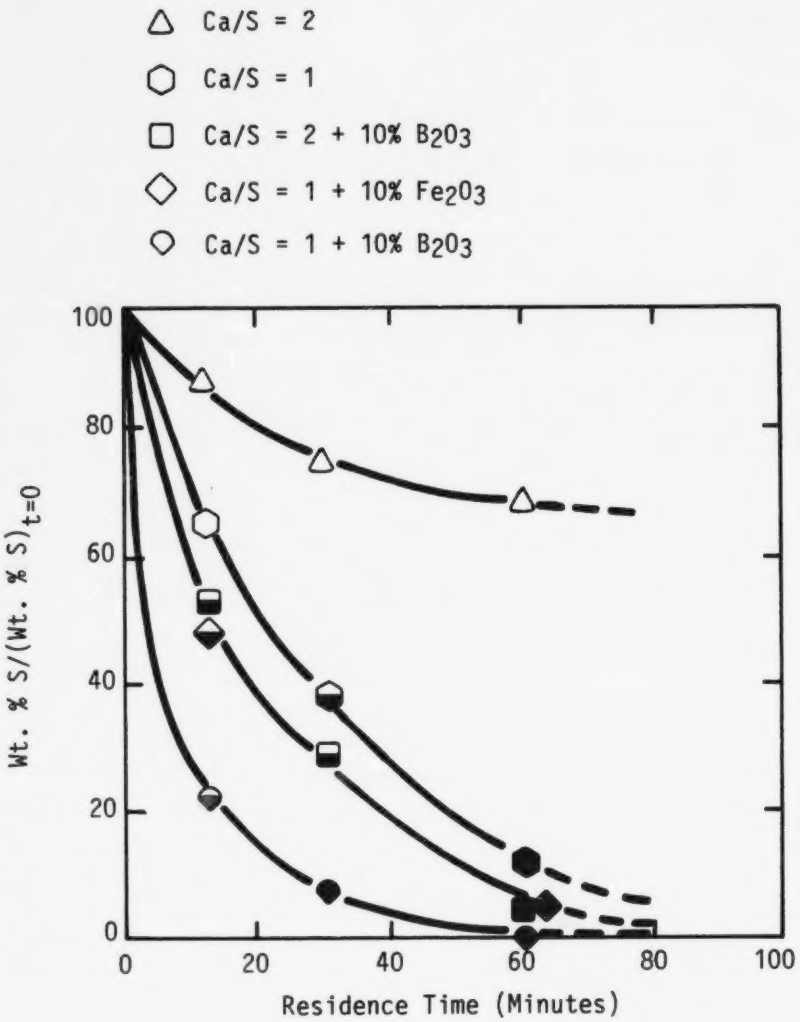


Figure 7-9. Desulfurization of CaS/Illinois coal ash/additive slag mixtures (open symbols represent completely unmelted samples, closed symbols correspond to completely melted samples).

$$\log [(\%S)_{equil.} - \%S] = \frac{P_{CO_2}}{(2.303)l} (k_2)t + I,$$

where P_{CO_2} is the partial pressure of carbon dioxide, l is the slag layer thickness, k_2 is the rate constant for the reaction:

$$S^{2-} + CO_2 \longrightarrow 1/2\ S_2 + CO + O^{2-}$$

and I is an integration constant. Figure 7-10 shows the desulfurization data on a semilogarithmic plot to allow the establishment of rate constants for the three well-mixed slag mixtures in Figure 7-8. Taking the sample thicknesses to be 1 mm and the partial pressure of CO_2 to be 0.049 atm, the rate constant for each mixture can be calculated and is presented in Table 7-3. In an actual precombustor system the slag layer thickness may be large enough to significantly slow the desulfurization process.

These results would indicate that fast slag drainage (less than 10 minutes) would be a desirable precombustor design feature. Another design option would be to avoid the formation of slag altogether by operating at lower temperatures and separating the ash and sorbent in a dry mode, but this approach has several practical drawbacks and is incompatible with most conventional slagging precombustors under development.

7.4 In Situ Sulfur Capture in Slag

The previous slag tests were carried out in a static oven facility in which premixed mixtures of Illinois coal ash and calcium compounds were exposed to a synthetic mixture of gases. A short test series was performed to investigate sulfur stability under an actual coal-fired slagging environment.

These tests were performed in the CTT at a firing rate of 23.4 kW (80,000 Btu/hr) using Illinois coal at a stoichiometric ratio of 0.6, identical to the test conditions used in establishing the entrained flow calcium utilization levels due to sulfidation presented earlier. Char, ash

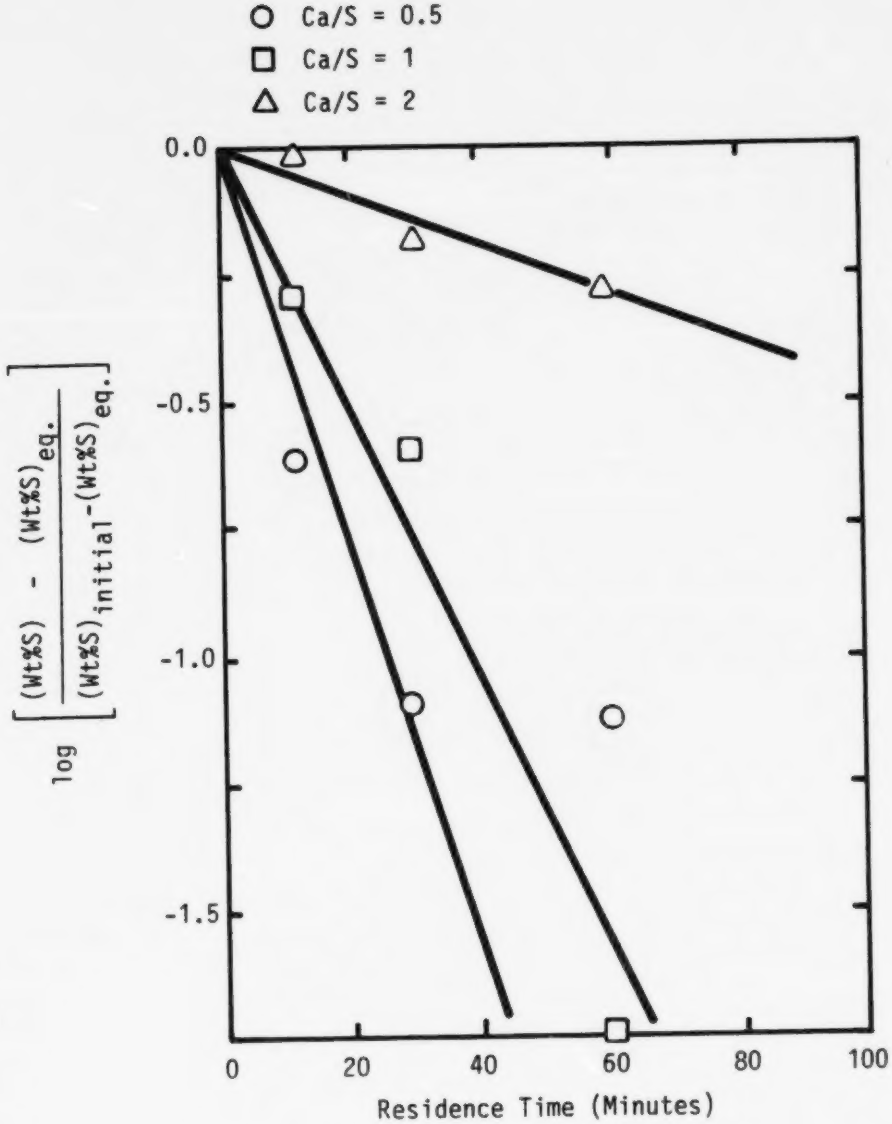


Figure 7-10. Desulfurization plot of CaS and Illinois coal ash mixtures plotted to obtain the rate constants presented in Table 7-3.

TABLE 7-3. DESULFURIZATION RATE CONSTANTS FOR CaS/ ILLINOIS COAL ASH MIXTURES

Ca/S	Wt.% Ca (as CaO)	k_2 $\left(\frac{\text{mm}}{\text{min - atm}}\right)$
0.5	26.89	1.88
1.0	42.14	1.22
2.0	58.81	0.218

and/or slag samples were collected by inserting two semicircular mullite channels (3.8 cm (1-1/2 inch) in diameter) positioned adjacent to each other across the 20.3 cm (8 inch) furnace duct. The concave portion of the ceramic channels were pointed upwards. The channels provided a projected cross-sectional area of 154.8 cm^2 (24 in^2). The channels were inserted at a distance of 86.4 cm (34 inches) downstream of the burner inlet. When sorbent was introduced into the furnace it was injected at a distance of 21.6 cm (8.5 inches) above the ceramic channels.

Results of sampling in the CTT under similar conditions presented earlier showed that approximately 75 percent of the carbon burned out at this location in the furnace. By placing the ceramic channels across the flow, a sample of char and ash gradually deposited. A layer of material about 1.3 cm (1/2 inch) thick deposited after an operating time of approximately 10 minutes. The light weight, fine particle samples were easily disrupted upon removal from the furnace by exhausting gases and thermal currents. To avoid this, the char was burned off before extraction from the furnace, leaving a solid ash deposit.

To simulate exposure to a fuel-rich, sulfur-laden exhaust stream without adding more particulate matter to the sample, the furnace was quickly switched from coal firing to an H_2S-doped natural gas flame. It was found that an exposure of from 2 to 3 minutes to the particle-free exhaust stream was sufficient to burn off the remaining carbon and leave ash and sorbent behind.

These results suggest that if the char material is deposited onto the walls of a precombustor chamber at similar stoichiometry and temperature, typical slag residence times would be sufficient for the remainder of the carbon to evolve.

At the sample location, previous testing had determined that the calcium utilization due to gas phase sulfidation reaction was on the order of 45 percent using Linwood atmospheric hydrate. By building up a slag sample on the ceramic channels with sorbent present and exposing the sample long enough to evolve all the carbon, an in situ measure of sulfur stability in the ash/slag was made.

First, tests were performed to establish required sampling conditions to assure complete burnout of the carbon. Preliminary tests were run without sorbent present and the following sampling procedure was established:

- 20 minutes firing Illinois coal
- 5 minutes firing H_2S-doped natural gas
- 20 minutes firing Illinois coal
- 5 minutes firing H_2S-doped natural gas

The sampling required two cycles in order to generate enough ash sample for elemental analyses. Without sorbent present, the carbon level was only 0.30 percent by weight while sulfur was 0.03 percent by weight.

The same procedure was then followed while sorbent was being injected (at Ca/S = 0.85). As expected from the slag fluidity testing, the samples with sorbent addition were more fluid than the ash sample without sorbent addition. However, there was a portion of the ash/sorbent sample that deposited near the sample port entrance that did not appear completely molten. This was due to cooler temperatures near the furnace wall and the high thermal conductivity of the mullite channels. There was a sufficient amount of the glass-like slag sample from the middle of the channels and the more metallic-like sample near the furnace wall to be analyzed separately. Elemental analyses of both samples were as follows:

	Glass-Like	Metallic-Like
Carbon (wt%)	0.67	0.10
Hydrogen	0.05	0.00
Sulfur	1.05	1.45
Calcium as CaO	29.57	36.44

The calcium utilization calculated for these two samples was 6.21 and 6.96 percent, respectively. These levels are far from the gas phase utilization levels determined earlier in the program, indicating that the sulfur regeneration observed in the static oven experiments also occurred in the more realistic conditions of the CTT. Note that the utilizations were fairly close to one other. This suggests that regeneration can take place in ash/CaS mixtures that are not completely fluid or glass-like.

8.0 QUALITY CONTROL EVALUATION

This section will summarize the results of the quality control/quality assurance (QA/QC) effort that was carried out throughout the performance of this program. Due to the nature of this program, it was classified as requiring a category IV QA/QC program. Experimental systems and sampling and analysis techniques were developed specifically for this program due to its unique requirements. A detailed discussion of the system sampling control measurements, sample analysis, calibration procedures and data reduction procedures are presented in Appendix A.

8.1 Instrument Accuracy and Precision

Table 8-1 presents accuracy and precision summaries for the continuous monitoring analyzers, the solids analysis instruments and techniques, and the gas chromatograph used in this program.

8.2 System Uncertainties and Data Completeness

As a measure of the representativeness of the data and system uncertainty, a series of sulfur balance experiments were performed on the ITR and the CTT facilities. To two standard deviations the balances varied 27 percent on the ITR and 15 percent on the CTT. These variances were used as combined uncertainty levels for the systems considering flow rate fluctuations, sampling system integrity, and analysis accuracy. Data that lay outside these uncertainty bounds were thrown out, resulting in data completeness of 90 percent for the ITR and 93 percent for the CTT.

The calcium utilization data presented in Section 6.0 are plotted along with approximate curve fits. All the data points lie within 27 percent and 15 percent of the plotted curves for the ITR and CTT data, respectively.

The relatively large uncertainty in the results is an indication of the difficulties involved in measuring sulfur species under reducing conditions. Several factors contributed to the ITR's increased uncertainty:

TABLE 8-1. PRECISION AND ACCURACY FOR ANALYSIS INSTRUMENTS AND TECHNIQUES

Measurement	Precision (%)		Accuracy (%)	
	Goal	Actual	Goal	Actual
Continuous Monitoring:				
NO_x	2	0.3	20	12.3
CO	2	0.5	20	No Std.
CO_2	2	0.1	20	2.5
O_2	2	0.2	20	13.1
SO_2	2	0.3	20	10.2
Sorbent and Fuel Composition:				
Carbon	2	0.24	2	0.8
Hydrogen	5	1.38	5	0.6
Nitrogen	10	2.13	10	1.9
Ash	10	0.33	10	1.42
Moisture	10	2.55	10	8.71
Sulfur	10	2.36	10	0.55
Calcium	10	1.0	10	0.2
Gas Chromatography:				
H_2S, SO_2, COS, CS_2	None Est.	4.8	None Est.	6.1

- The ITR's small scale caused greater flow control uncertainty.

- The GC was located on a different site than the ITR, making sample storage time longer for the ITR samples.

- The ITR testing was performed prior to the CTT testing so that experience gained in sampling reduced sulfur species helped improve data quality during the CTT testing.

The HTO was, for the most part, a static facility. That is, samples were preloaded and sat stationary in the oven for long time intervals as opposed to the dynamic injection and sampling tests performed on the ITR and CTT. As a consequence, data uncertainty was dominated by the accuracy and precision of the solids analysis instruments and techniques which are presented in Table 8-1. Completeness for the HTO data was 100 percent.

9.0 CONCLUSIONS

The investigations described in this report have been aimed at understanding the sulfur capture process using calcium-based sorbents under fuel-rich precombustor conditions and how the other precombustor processes (such as carbon burnout, particulate emissions and NO_x control) are impacted by the sulfur capture process. The major findings of this program can be summarized as follows:

- Under fuel-rich conditions, CaO reacts very quickly with H_2S and to a much higher level than CaO and SO_2 under corresponding fuel-lean conditions.

- At fuel-rich conditions that favor high carbon burnout (high temperature, near stoichiometric), gas phase sulfur is present mainly as SO_2.

- Substantial concentrations of H_2S can be generated when firing coal under deep substoichiometric conditions (SR = 0.6).

- Sulfur capture is enhanced by injection of sorbent into lower temperature regions (less than 1300°C (2372°F)), probably due to less sorbent sintering when exposed to lower temperatures.

- Typical molten coal ash and mixtures of coal ash and CaO are incapable of holding large amounts of sulfur in a coal precombustor environment when at equilibrium.

- Large amounts of Fe_2O_3 can help reduce the melting temperature of slag and increase the slag sulfur capacity but may be technically difficult to implement and economically impractical.

- Coal ash/CaO slags rapidly desulfurize from super-equilibrium levels of sulfur at precombustor temperatures and gas compositions.

- B_2O_3 is an effective slag fluxing additive for coal ash CaO mixtures.

The data collected within this program has indicated that there are several imposing obstacles to overcome before sulfur control can be achieved in conventional precombustor systems. However, there is much cause for optimism that with additional work at the pilot scale a feasible precombustor system with sulfur control can be designed. According to the information generated within this program, new precombustor designs for the control of sulfur emissions should promote the following:

- High levels of H_2S and COS to feed the fast fuel-rich reaction with CaO, potentially by deep substoichiometric operation and longer residence times.
- Sorbent injection into lower temperature regions (i.e., avoidance of flame fronts) of the combustor to help generate a very reactive sorbent.
- Long fuel residence times to achieve high carbon burnout.
- The use of slag fluxing additives to extend the operable temperature range within slagging precombustors.
- Slag drainage designs which promote quick removal of the sulfur laden slag before extensive desulfurization can occur.
- Alternatively, low temperature operation with dry solids rejection to avoid slag formation and slag desulfurization.

10.0 RECOMMENDATIONS

The testing performed in this program has provided important process information that can be used in applying fuel-rich sorbent injection to existing precombustors and other combustion systems. The results have been favorable enough to merit further process evaluation and investigation at the pilot scale. It is recommended that a test sequence be performed on existing precombustor systems (such as EER's 3 MW_t (10×10^6 Btu/hr) VCC system).

Testing should include variations in stoichiometry, load (affecting residence time), temperature, injection location, coal type, and sorbent type. Also, use of slag fluxing additives and variations in slag drainage design should be investigated.

Measurements to be made should include:

- Internal sulfur speciation;
- Downstream SO_2 concentration;
- Calcium utilization (measured internally and by downstream SO_2 change);
- Carbon burnout;
- Slag drainage consistency;
- Particle separation efficiency; and
- Slag and fly ash composition.

The potential exists that significant entrained flow sulfur capture through calcium sulfidation can occur in precombustor systems while still maintaining fluid slag and high carbon burnout. Of less certainty is the fate of the CaS as it makes its exit from the precombustor. If the CaS particles come into contact with a slag layer it may be drained fast enough to avoid significant desulfurization. This process is very difficult to test on bench scale facilities and is likely to vary substantially with precombustor design.

The information generated by this program also allows other full scale testing on precombustor systems to be evaluated properly in terms of analysis techniques and operating conditions. For some time there has been questions as to the validity of some of the claims made by precombustor researchers - claims made without proper substantiation. It is recommended that those claims be evaluated in light of the results of this program and that any further testing proceed in an informed fashion.

11.0 ACKNOWLEDGMENTS

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APPENDIX A

QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

The collection and analysis of quality data has been of upmost importance to this program. In order to ensure that the reported data is accurate, many quality assurance measures have been taken in all phases of the program. This program was classified as requiring a category IV QA/QC program due to its exploratory research nature. Most of the procedures and measurements used for data acquisition haven been standardized by EPA or ASTM and those which have not are described in detail in this appendix.

Three facilities at EER were involved in obtaining the data presented in this report; the ITR, CTT and HTO (discussed in detail in Section 5.0). Unless stated otherwise, all of the quality assurance information presented in this appendix applies to all three facilities.

A.1 Experimental Systems

A.1.1 Gas Species Sampling

Exhaust gas-phase species composition was measured using the ITR and CTT laboratory sampling systems. These systems were constructed in strict conformance with EPA performance specifications and their use helped ensure data quality. The species that were measured continuously included: NO, NO_x, SO_2, CO, O_2, and CO_2. Batch gas (GC) samples were collected for analysis of H_2S, COS, SO_2, and CS_2 by gas chromatography.

Figure A-1 shows a schematic diagram of the continuous monitoring system for NO, NO_x, CO, CO_2, and O_2 used on the CTT. The system was similar for both the ITR and CTT. All components in contact with the sample were stainless steel or Teflon to ensure sample integrity and corrosion resistance. The gas sample was provided to the instruments by a sample conditioning system consisting of a pump, moisture condenser and particulate filters.

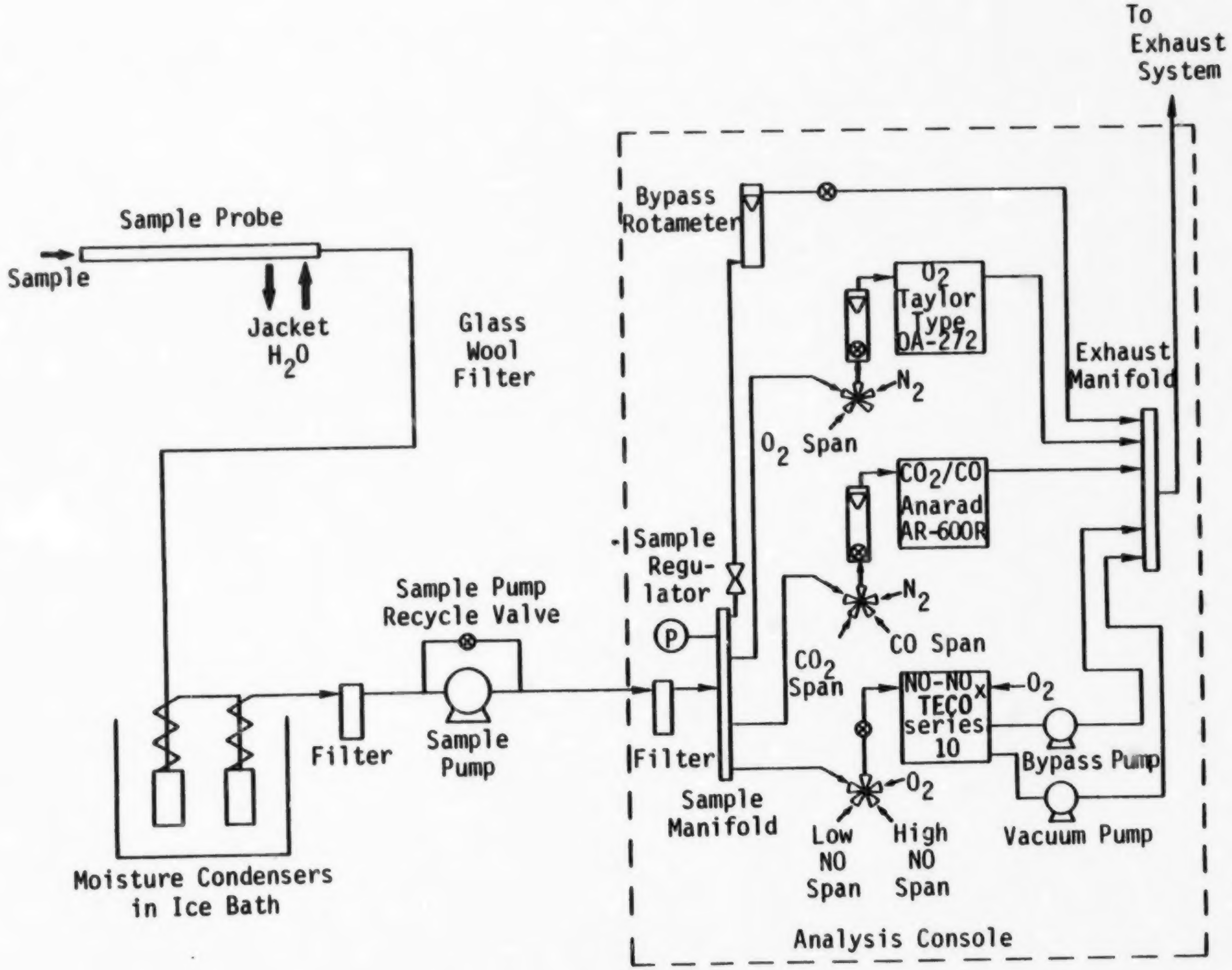

To Exhaust System
Sample Probe
Sample
Jacket H_2O
Glass Wool Filter
Bypass Rotameter
O_2 Taylor Type OA-272
Exhaust Manifold
N_2
O_2 Span
CO_2/CO Anarad AR-600R
Sample Regulator
N_2
CO Span
Sample Pump Recycle Valve
P
CO_2 Span
$NO-NO_x$ TECO series 10
O_2
Filter
Sample Pump
Filter
Bypass Pump
O_2
Sample Manifold
Low NO Span
High NO Span
Vacuum Pump
Moisture Condensers in Ice Bath
Analysis Console

Figure A-1. Continuous monitoring flue gas sampling system.

Gas phase measurements were made routinely at the exhaust of the ITR and CTT to assure steady operating conditions. Phase discrimination probes (see Figure A-2) were used in both facilities for measurement of sulfur species in the exhaust. The probes supplied two gas streams simultaneously. The main, particle-laden stream was used for continuous monitoring of O_2, CO, CO_2, NO_x, and the nearly particle-free side stream was used for SO_2 measurement and for collection of batch samples for GC analysis.

Figure A-3 shows a diagram of the continuous monitoring system for exhaust SO_2 measurements. The SO_2 gas sample in the nearly particulate-free stream was transported in a heated Teflon line maintained above 100^oC under vacuum to a heated filter followed by a permeation tube drier. The permeation tube drier selectively removed water vapor from the gas sample. Dry air was used as the dry gas medium in the permeation drier. The sample was then pressurized and delivered to the analyzer.

The same system was used for collection of samples for GC analysis. Once again, the permeation tube drier was used to prevent contact between the exhaust gases and condensated water. An investigation by Cassidy (1974) showed that the tubing material was not permeable to either SO_2 or H_2S. Tedlar sample bags were used to collect the gaseous sample and for storage until analysis in the GC. A septum fitting on the sample bag allowed removal of the necessary sample by syringe. Syringe injection was selected over use of a flow valve for introduction of the sample to the GC to allow wider calibration ranges and to minimize contacting with stainless steel to avoid adsorption of sulfur species.

The tedlar bags were leak checked before testing began. After several usages some bags were filled with pure N_2 and submitted for GC analysis as blanks. All of these cases failed to show measurable levels of sulfur species. Besides testing the GC with a blank sample, this also indicated that negligible amounts of sulfur species were absorbing onto the bags and released later.

Dimensions: Inches

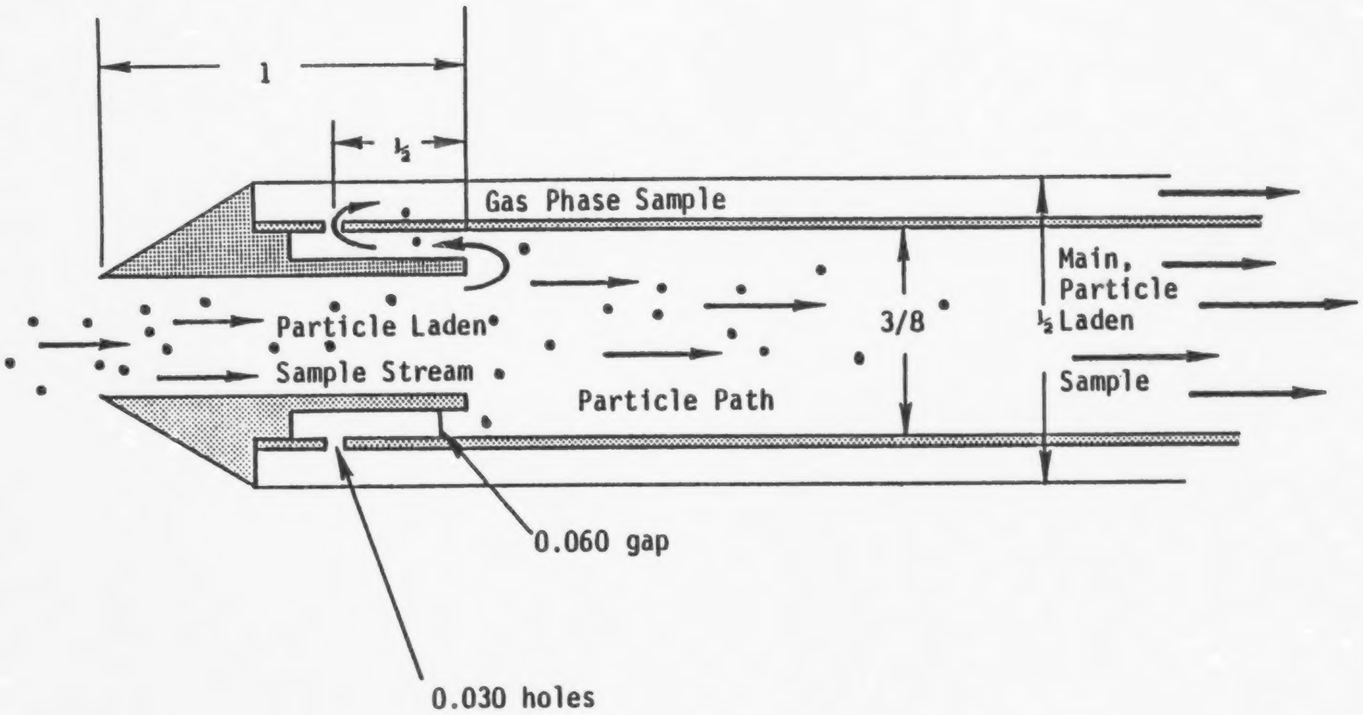

1
½
Gas Phase Sample
Particle Laden
Sample Stream
Particle Path
3/8
½
Main,
Particle
Laden
Sample
0.060 gap
0.030 holes

Figure A-2. Phase discrimination probe tip.

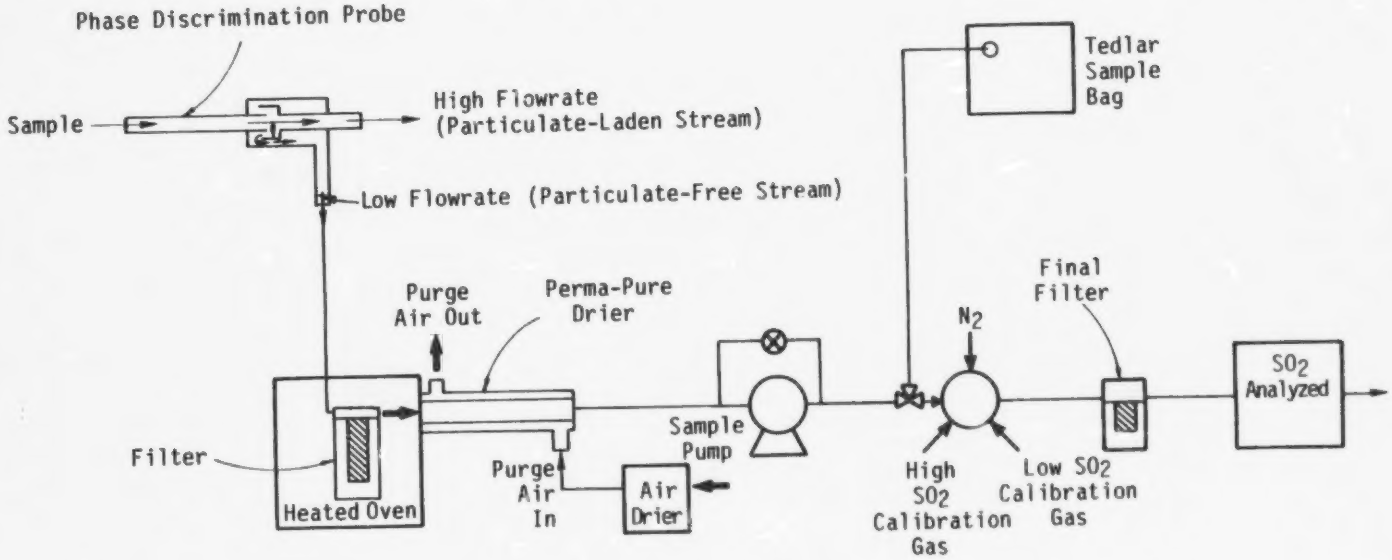

Phase Discrimination Probe
Sample
High Flowrate (Particulate-Laden Stream)
Low Flowrate (Particulate-Free Stream)
Purge Air Out
Perma-Pure Drier
Filter
Heated Oven
Purge Air In
Air Drier
Sample Pump
Tedlar Sample Bag
N_2
High SO_2 Calibration Gas
Low SO_2 Calibration Gas
Final Filter
SO_2 Analyzed

Figure A-3. SO_2 continuous monitoring and batch sampling system.

Figure A-4 shows results of a test to establish the maximum storage time in a sample bag before analysis. A conservative value of two hours was used throughout the testing on the CTT and four hours on the ITR (the ITR is located at a different location than the GC and the CTT).

A.1.2 Solids Sampling

Solids were collected in the ITR facility with the system shown schematically in Figure A-5 and in the CTT facility with the system shown in Figure A-6. Both systems were operated with the capability of monitoring the gas sample temperature to assure that no condensation occurred within the probe or filter housing. To test whether additional sulfur was captured by the sampled sorbent while sitting on the sample filter, an H_2S laden, fuel-rich gas stream was pulled over a preloaded precalcined sorbent (with a surface area of 32 m^2/g) and a raw calcium hydroxide sample in the solids sampling probe. For both the ITR and CTT, less than one percent of the calcium was utilized through reaction with sulfur when tested at typical sample duration times. Each solids analysis was performed using all the collected sample to avoid the question of sample representativeness.

A.1.3 Temperature Measurements

High temperature gas measurements within furnaces are subject to large inaccuracies due to the effects of thermal couple radiation loss. Therefore, in-furnace gas temperatures were measured using a fine-wire thermo-couple on the ITR and a suction pyrometer on the CTT.

The fine-wire thermocouple was made with 0.025 mm diameter type-S thermocouple wire, butt-welded across a forked support. Temperature readings in degrees Celsius were obtained with an electronic readout containing an internal icepoint reference. The specified accuracy of the readout was ± 2.3°C. Figure A-7 presents a diagram of the fine-wire thermocouple.

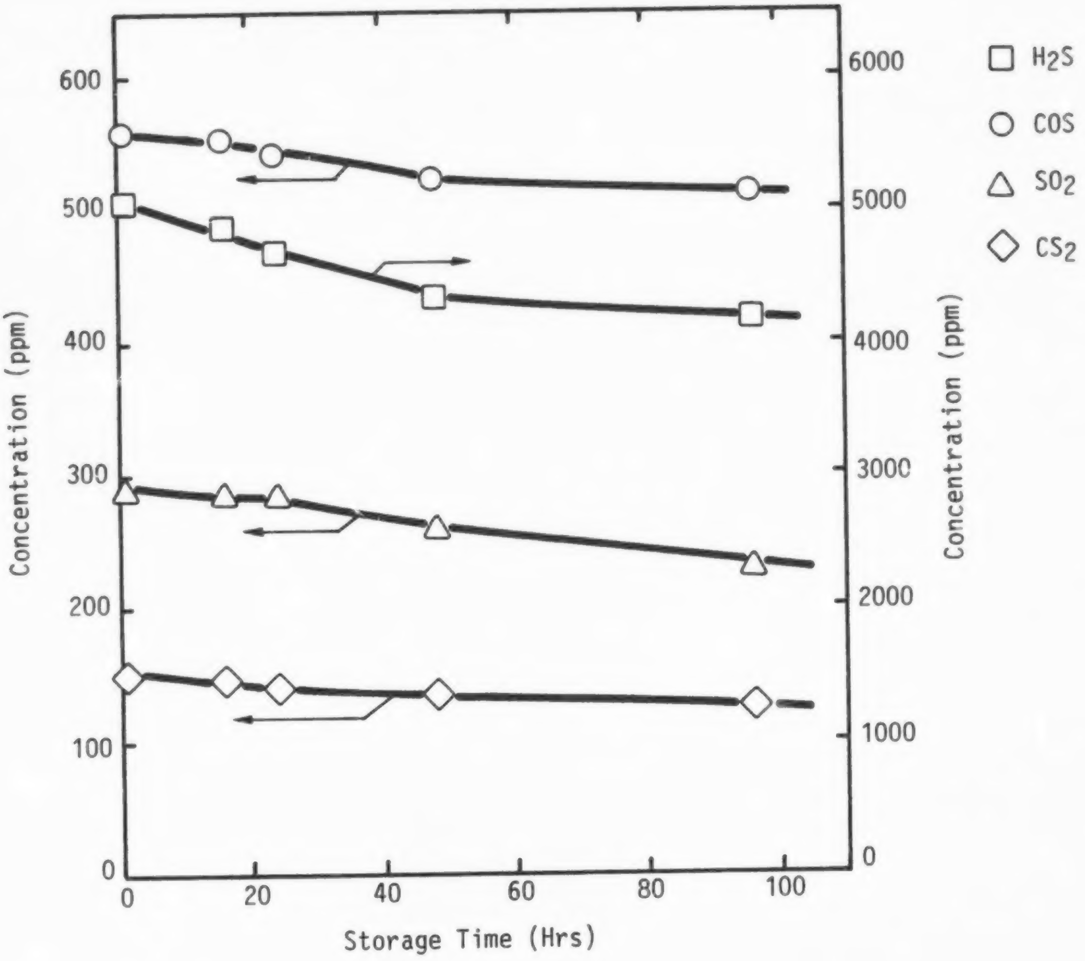


Figure A-4. Depletion of sulfur species within a tedlar sample bag as a function of storage time.

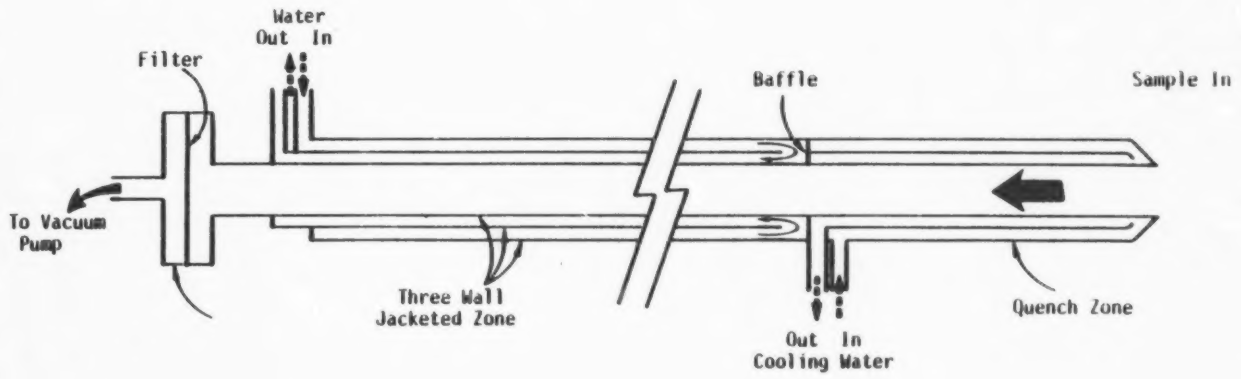

Water
Out In
Filter
Baffle
Sample In
To Vacuum Pump
Three Wall Jacketed Zone
Out In
Cooling Water
Quench Zone

Figure A-5. Isokinetic solids sampling probe with upper and lower cooling jackets used in the ITR.

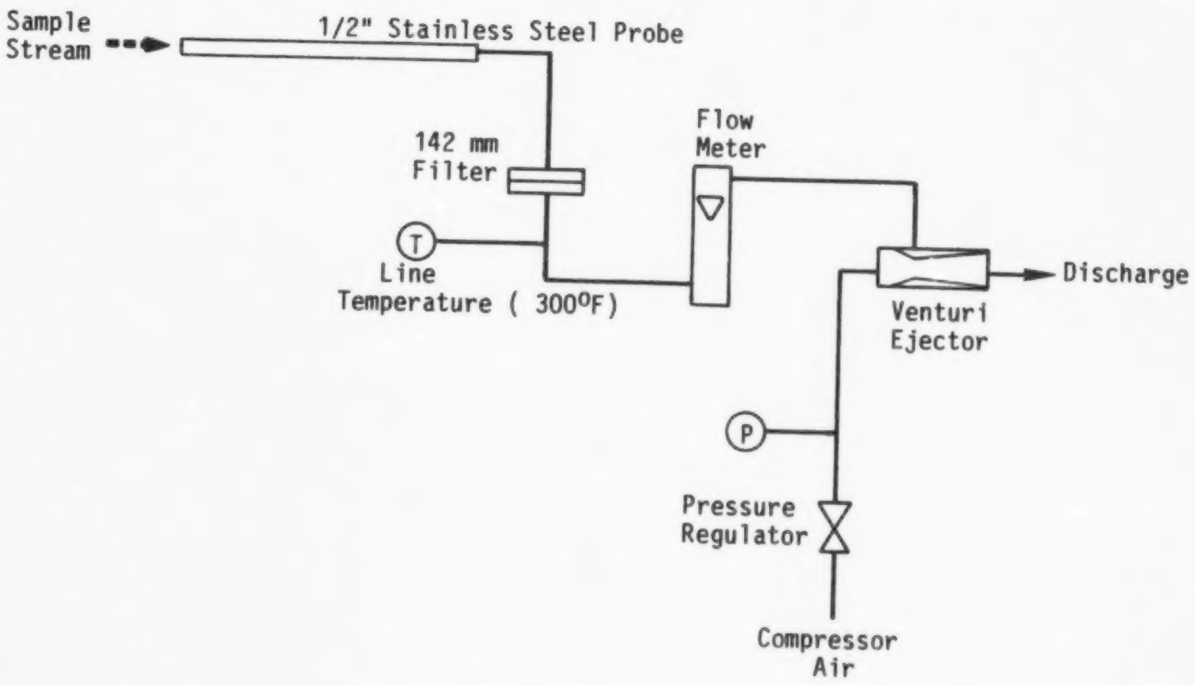

Sample Stream
1/2" Stainless Steel Probe
142 mm Filter
T
Line Temperature (300°F)
Flow Meter
Venturi Ejector
Discharge
P
Pressure Regulator
Compressor Air

Figure A-6. Solid sampling system used on the CTT.

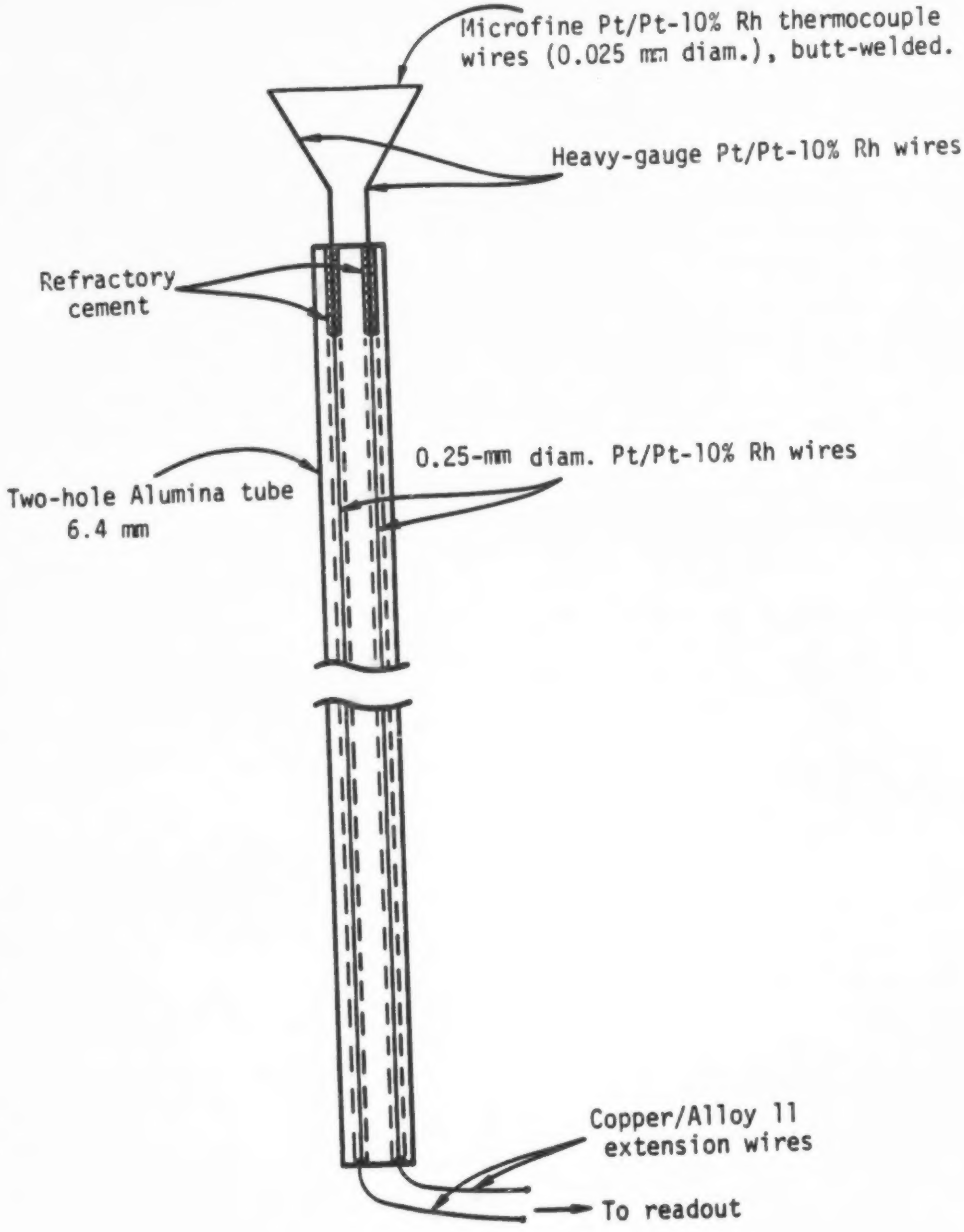

Microfine Pt/Pt-10% Rh thermocouple wires (0.025 mm diam.), butt-welded.
Heavy-gauge Pt/Pt-10% Rh wires
Refractory cement
0.25-mm diam. Pt/Pt-10% Rh wires
Two-hole Alumina tube 6.4 mm
Copper/Alloy 11 extension wires
To readout

Figure A-7. Fine-wire thermocouple probe for gas temperature measurements in the ITR.

The fine wire thermocouple was utilized in order to minimize the uncertainties of radiation corrections. Radiation corrections to the thermocouple readings were determined by balancing the equations for heat transfer away from the thermocouple wire:

$$q_{conv} = h_o A (T_{tc} - T_{gas}) \tag{A-1}$$

$$q_{rad} = \epsilon \sigma A (T^4{}_{tc} - T^4{}_{env}) \tag{A-2}$$

where:

q_{conv} = convective heat loss
q_{rad} = radiative heat loss
h_o = convective heat transfer coefficient
A = surface area per unit length of t.c. wire
T_{wire} = t.c. wire temperature, K
T_{gas} = gas temperature, K
T_{env} = temperature of surroundings, K
ϵ = emissivity of platinum, $\epsilon = 0.18$
σ = Stefan-Boltzman constant

The heat transfer coefficient was determined by the equation:

$$\frac{h_o D_o}{k_f} = \left(\frac{C_p \mu}{k_f}\right)^{0.3} \left[0.35 + 0.56 \left(\frac{\rho V D_o}{\mu}\right)^{0.52}\right] \tag{A-3}$$

where:

D_o = t.c. wire diameter
k_f = gas thermal conductivity
$\frac{C_p \mu}{k_f}$ = Prandtl number, 0.7
$\frac{\rho V D_o}{\mu}$ = Reynolds number, 0.1

Solving these equations yielded $h_o = 4.4 \times 10^{-2}$ cal·cm^{-2}·s^{-1}·K^{-1}. Setting equations A-1 and A-2 equal to each other:

$$T_{gas} = T_{wire} + \frac{(T^4_{wire} - T^4_{env})}{1.79 \times 10^{11}} \quad \text{(A-4)}$$

where T_{env} is taken as the wall temperature of the ITR. The correction is significant (>5 K) only when the thermocouple temperature differs from the ITR temperature by more than about 75 K. Which was never the case during this test sequence.

Radial temperature gradients in the ITR were small while operating under isothermal conditions. Table A-1 shows how the temperature varied from the center of the ITR at 900°C under fuel-lean conditions. The reactor was divided into four quadrants which were labeled by their closest compass points: N, S, E, and W. The temperature was measured "near the wall" in each direction away from the ITR axis. In all but two cases, duplicate measurements were made.

The temperature of the ITR itself was monitored by a programmable control unit using four type R (Pt/Pt-13 percent Rh) thermocouples. These thermocouples are normally stable and were at no time subjected to the reactive flame gases. Therefore, they were not checked for deterioration during the course of the experimental work.

The suction pyrometer system used on the CTT is presented in Figure A-8. The suction pyrometer consisted of a high-temperature thermocouple (B type) in a porous ceramic radiation shield. The pyrometer was placed in the gas stream with the opening in the alumina sheath pointing downstream. A high flow rate of furnace gas was drawn through the sheath and over the thermocouple to increase convective heat transfer to the thermocouple and reduce radiation loss. As the gas flow rate was increased, the gas temperature increased to a constant value, indicating no additional reduction in radiation loss. Figure A-9 shows the results of the ejector pressure (a measure of flow rate through the pyrometer) calibration for the CTT. An

TABLE A-1. RADIAL TEMPERATURE CHANGE IN THE ITR AT A NOMINAL 900°C ISOTHERMAL CONDITION

Distance from Burner, cm	Temperature, °C Axis	N	S	E	W
107	897	895	895	899	895
94	909	910	911	910	910
	905	906	904	904	900
81	904	907	909	906	910
	903	905	906	902	905
69	903	902	908	904	906
	904	906	911	910	913
56	903	902	912	901	907
	909	908	916	913	912
43	903	902	910	909	906
	902	904	906	903	909
30	900	898	896	902	898

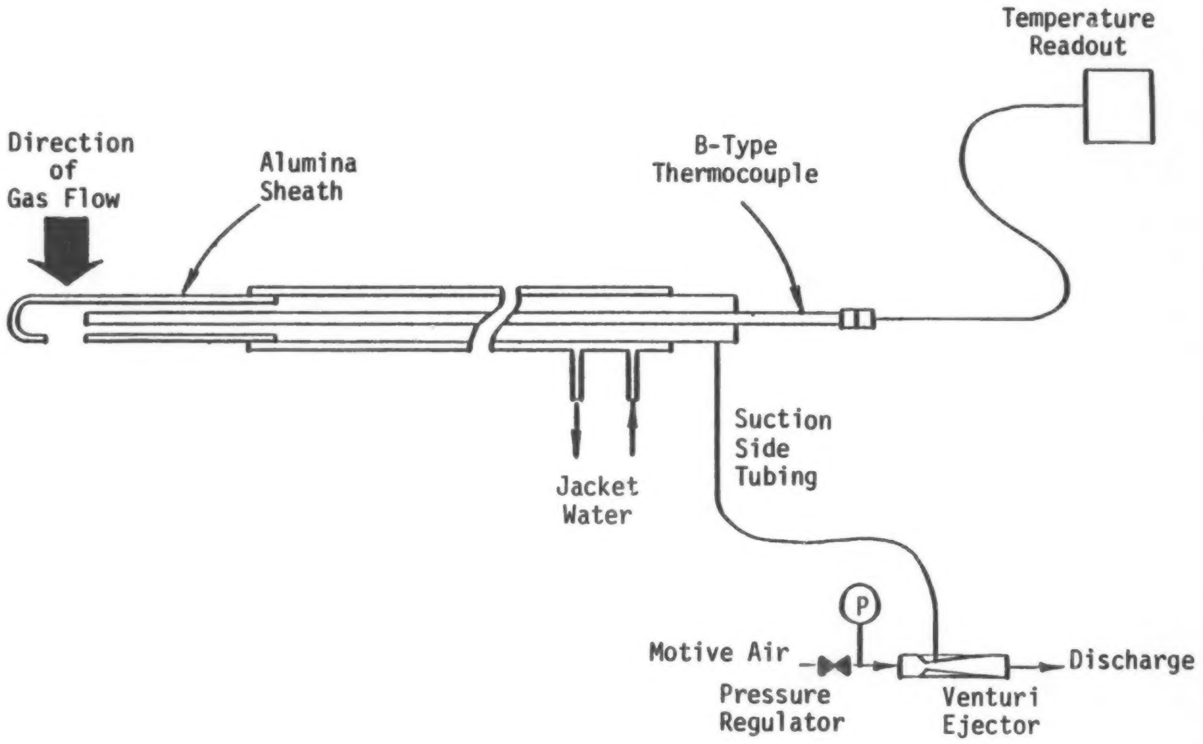

Temperature Readout
Direction of Gas Flow
Alumina Sheath
B-Type Thermocouple
Suction Side Tubing
Jacket Water
P
Motive Air
Pressure Regulator
Venturi Ejector
Discharge

Figure A-8. Gas temperature measurement system for the CTT.

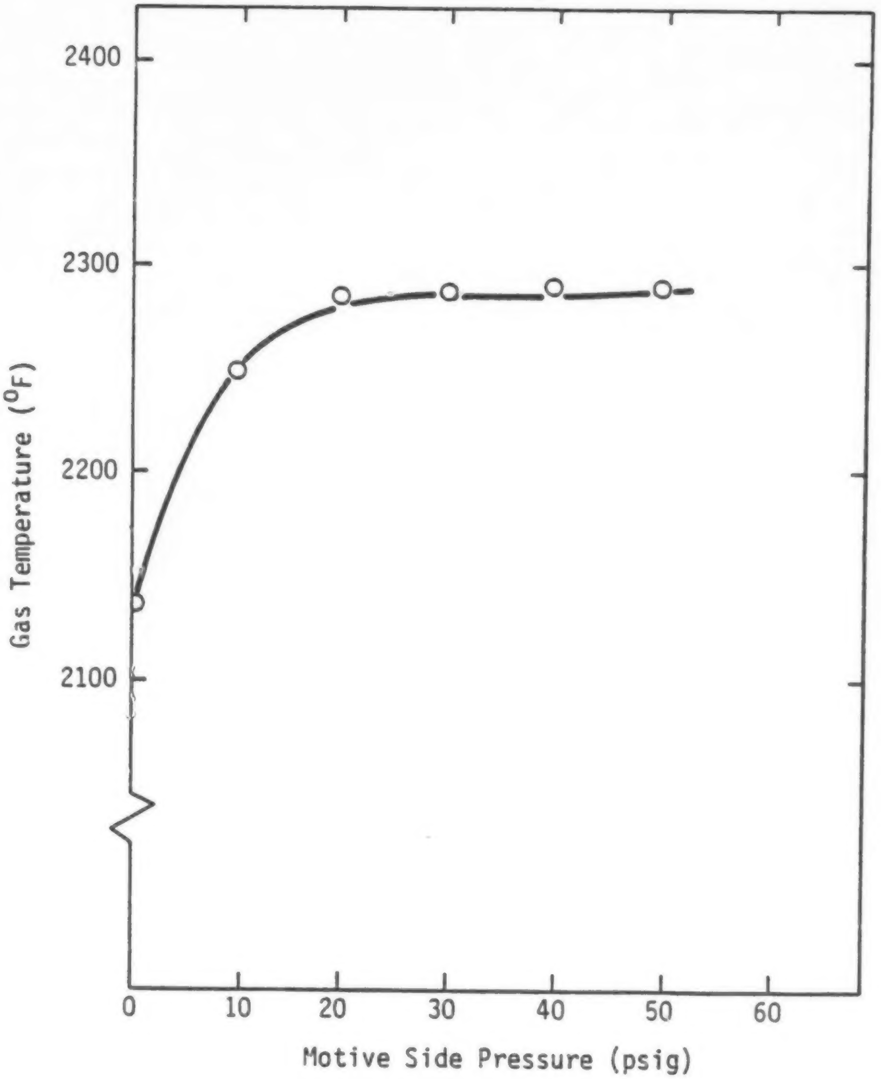


Figure A-9. Suction pyrometer aspirator pressure calibration for CTT.

operating pressure of 40 psig was adopted for all the temperature measurements for the CTT system.

A.1.4 Gas Flow Metering

All gas flow rates were measured by suitably sized rotameters. The rotameters were calibrated using air with venturi and laminar flow element flow meters. Flow rates were corrected for pressure and specific gravity (relative to air) using the formula:

$$Q = Q^{o} \left[\frac{P}{101.3\text{kPa}} \times \frac{1}{\text{S.G.}} \right]^{1/2} \qquad \text{(A-5)}$$

where:

Q = true flow rate
Q^{o} = measured flow rate
P = outlet rotameter pressure, kPa
S.G. = gas specific gravity

H_2S dopant flow rate was compared to the measured SO_2 concentration at the exhaust when operating fuel-lean to assure a proper initial dopant feed rate.

A.1.5 Sorbent Feed Rate

The sorbent feed rate was measured by feeding sorbent directly into a tared sample jar and weighing the accumulated sorbent after a measured discharge time. This was done before and after each test to assure a steady sorbent feed. If the feed rate calibration varied more than 10 percent from before to after, the test was repeated. Typically sorbent feed rates fluctuated less than five percent.

A.2 Analytical

A.2.1 Continuous Gas Species Analysis

Table A-2 lists the specific instruments and full-scale ranges for the continuous monitoring system. The instrument ranges were selected to exceed the maximum expected concentrations by a small margin.

Table A-3 gives the precision, accuracy, and completeness information for the continuous monitoring instruments used on the ITR and CTT. In every case, the program goals for precision and accuracy were met.

A.2.2 Gas Chromatography Analysis

Gas chromatograph (GC) analysis of fuel-rich exhaust gases for measurement of H_2S, COS, SO_2 and CS_2 was performed with a Perkin Elmer 2 gas chromatograph using a Supelco Chromasil 310 column and a flame photometric detector.

The GC was checked at least twice daily with span gases of known specie concentration. Figure A-10 presents the variation of this standard check over a single calibration period. The precision and accuracy of the data (to two standard deviations) was established to be 4.8, and 6.1 percent, respectively for the GC analyses.

A.2.3 Solids Analysis

The composition of solid samples was generally determined by EER's Analytical lab though some samples were sent to an independent laboratory. Carbon, hydrogen and nitrogen were analyzed on a Perkin-Elmer 240B and solid sulfur species were determined from a Leco SC32 Analyzer. Calcium analysis was done with a Chelometric titration method which is covered under ASTM D 2795. Table A-4 gives the precision and accuracy data for these instruments and methods.

TABLE A-2. CTT INSTRUMENTATION

Gas Measured	Type of Instrument	Manufacturer	Model No.	Range	Reference
NO, NO_x	Chemiluminescent	Thermo Electron Corp. (TECO)	10 Ar	1000 RPM	Teco Model 10 Operating Manual
CO	Nondispersive Infrared (NDIR)	Anarad, Inc.	AR600R	10 Percent	Anarad AR 600 Operating Manual
CO_2	Nondispersive Infrared (NDIR)	Anarad, Inc.	AR600R	40 Percent	Anarad AR 600 Operating Manual
O_2	Paramagenetic	Taylor Servumex	OA250	100 Percent	Taylor OA250 Operating Manual
SO_2	UV Absorption	DuPont	400	5000 ppm	DuPont 400 Operating Manual

TABLE A-3. PRECISION, ACCURACY AND COMPLETENESS DATA FOR CONTINUOUS MONITORING GAS SPECIES INSTRUMENTS

Gas Measured	Precision (%)		Accuracy (%)		Completeness (%)	
	Goal	Actual	Goal	Actual	Goal	Actual
NO_x (Chemiluminescent)	2	0.3	20	12.3	90	100
CO (NDIR)	2	0.5	20	No Std.	90	100
CO_2 (NDIR)	2	0.1	20	2.5	90	100
O_2 (Paramagentic)	2	0.2	20	13.1	90	100
SO_2 (UV Absorption)	2	0.3	20	10.2	90	100

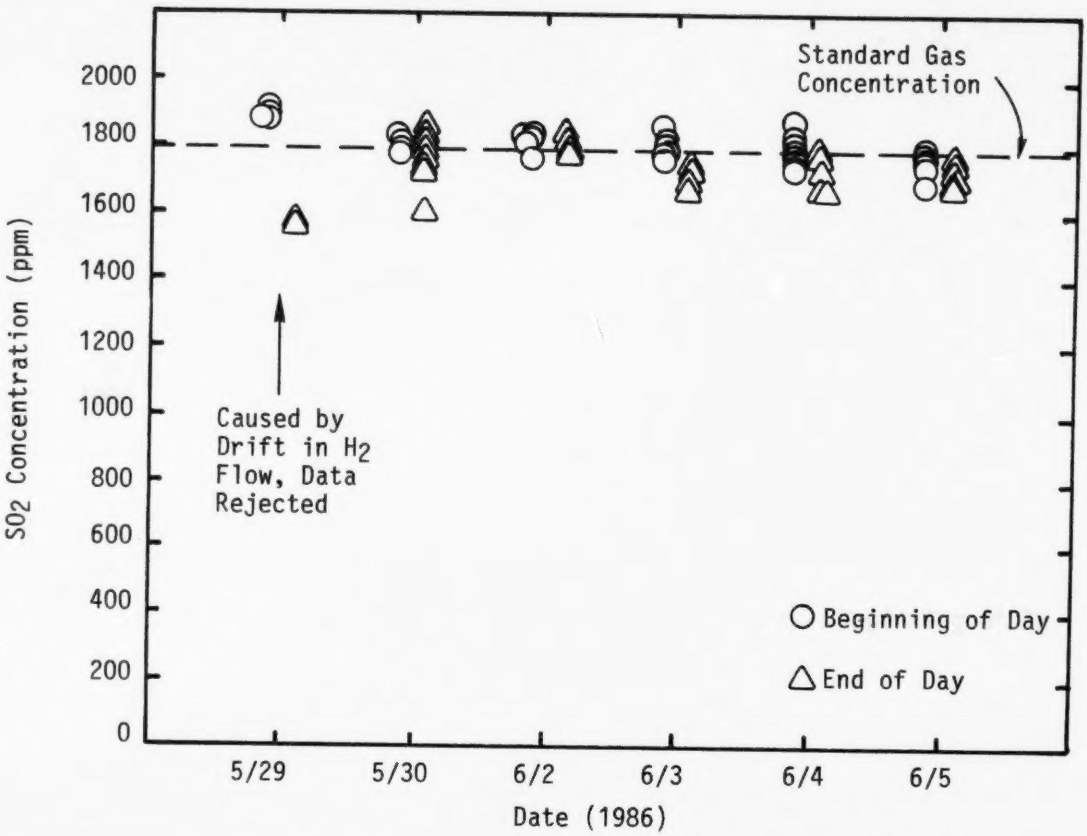


Figure A-10. Example of daily standard checks for the gas chromatograph during one calibration period.

TABLE A-4. SOLID ANALYSES PRECISION AND ACCURACY DATA

Measurement	Precision (%)		Accuracy (%)	
	Actual	Goal	Actual	Goal
Carbon	.24	2	0.8	2
Hydrogen	1.38	5	0.6	5
Nitrogen Perkin-Elmer 240 B	2.13	10	1.9	10
Ash	0.33	10	1.42	10
Moisture	2.55	10	8.71	10
Sulfur - Leco SC32	2.36	10	0.55	10
Calcium - ASTM D2795	1.0	10	0.2	10

Ash fusion temperatures were determined by an independent laboratory (determined by competitive evaluation between three laboratories) with a method covered under ASTM D 1857. The laboratory participates in a monthly round robin quality control service. The fluid temperature precision and accuracy were determined to be 0.6 and 2.1 percent, respectively for the months in which samples from this program were analyzed by the lab.

Slag samples were first pulverized before analysis in the sulfur analyzer. An oxidizing additive (vanadium pentoxide) was added to the test slags as recommended by Leco to assure that all the sulfur evolved from the slag.

A.2.4 Data Representativeness and Completeness

The previous subsections have discussed instrument accuracy and precision. As a measure of total uncertainty in the data associated not only with instrument uncertainty but also system fluctuations, sulfur balances were made for each test condition. System uncertainties included dopant sulfur feed rate; coal, air and sorbent feed rates; sample train leakage; sample bag leakage; instrument reading fluctuations; etc. Also, data completeness has been determined based on the number of reported data points compared to the number of data points taken (excluding all data that was rejected due to identified feeding, sampling or analysis problems).

Sulfur balances on the ITR varied 27 percent (two standard deviations), and completeness of the data was 90 percent. On the CTT, sulfur balances when firing coal were within 15 percent (again, two standard deviations) and completeness was 93 percent. The data presented in Sections 6.0 all lie within these sulfur balance uncertainties. That is, the curves drawn through the data points are within 27 and 15 percent of the plotted data points for the ITR and CTT, respectively. Data points that laid outside of these established uncertainty ranges were thrown out and contribute to the reported completeness levels of 90 and 93 percent.

The HTO facility system uncertainty was very low since the samples were preloaded and sat stationary for a long furnace exposure time. The largest uncertainties were associated with the solids sampling accuracy and precision reported in Section A.2.3. Completeness of the HTO data was 100 percent.

A.3 Calibration Procedures

Calibration procedures and frequency for all standard measurement systems are listed in Table A-5. As shown in the table, standard calibration procedures were used for each system. Each system was calibrated at the frequency shown in the table to ensure that the accuracy of the measurement could be traceable to the calibration standards.

Each of the continuous monitoring instruments was calibrated with three gases: a zero gas and two span gases. Table A-6 lists the span gases used to calibrate instruments for the CTT sample system.

Calibration of the GC was performed by evacuating an 11 liter glass chamber, injecting a known quantity of pure compound (H_2S, SO_2, COS or CS_2), and filling up the remainder of the chamber with ambient air. Then, by injecting different volumes of gas into the GC, the detector response was recorded. In this way, the optimum instrument sensitivity could be achieved for each sulfur specie. This was repeated at several concentrations ranging up to 5000 ppm for H_2S and SO_2, 1500 ppm for COS, and 1000 ppm for CS_2. Figures A-11 through A-14 show the calibration curves used for the majority of the data presented in this report.

Calibrations were performed immediately before each major testing sequence and were checked daily to assure accuracy.

Figures A-15 through A-17 present examples of the gas chromatograph readout. The peaks are sharp and clean. The flattened peaks of Figure A-15 are due to the attenuation setting of the printout equipment and not due to oversaturation of the sulfur detector. The integrated values for the peaks

TABLE A-5. CALIBRATION PROCEDURES

Measurement Parameter	Calibration Procedure	Calibration Frequency	Calibration Standard	Reference
Fuel Composition:				
Carbon	Standard Samples	Daily	Known quantity of 100% acetanilide	Perkin Elmer 240 B Operating Manual
Hydrogen				
Nitrogen				
Ash				
Moisture				
Sulfur	Standard Sample	Daily	Certified sulfur standards	Leco SC 32 Operating Manual
Exhaust Gas Composition				
NO, NO_2	Compare to standard compressed gas	Daily	EPA Protocol 1 Gases or custom gas blends. See Section 10.0	EPA EMSL Protocol No. 1, June 1, 1978
O_2				
CO				
CO_2				
SO_2				
Hydrocarbons				
Sorbent Surface Area		Daily	Known quantity of N_2	Quantasorb Surface Area Analyzer Operating Manual
Sorbent Flowrate	Weigh feed over measured time with independent balance	Before and after each run	Standard weights	

TABLE A-6. CALIBRATION GASES

Gas	Concentration	Percent of Full-Scale	Balance Gas	Grade
NO	836 ppm	84	Nitrogen	Certified Standard
NO	166 ppm	16	Nitrogen	Certified Standard
SO_2	2915 ppm	73	Nitrogen	Certified Standard
SO_2	437 ppm	11	Nitrogen	Certified Standard
CO	1227 ppm	82	Nitrogen	Certified Standard
CO_2	12.3%	31	Nitrogen	Certified Standard
CO_2	5%	13	Nitrogen	Certified Standard
O_2	10%	10	Nitrogen	Certified Standard
O_2	4%	4	Nitrogen	Certified Standard
CO	10%	100	Nitrogen	Certified Standard
CO	2%	20	Nitrogen	Certified Standard

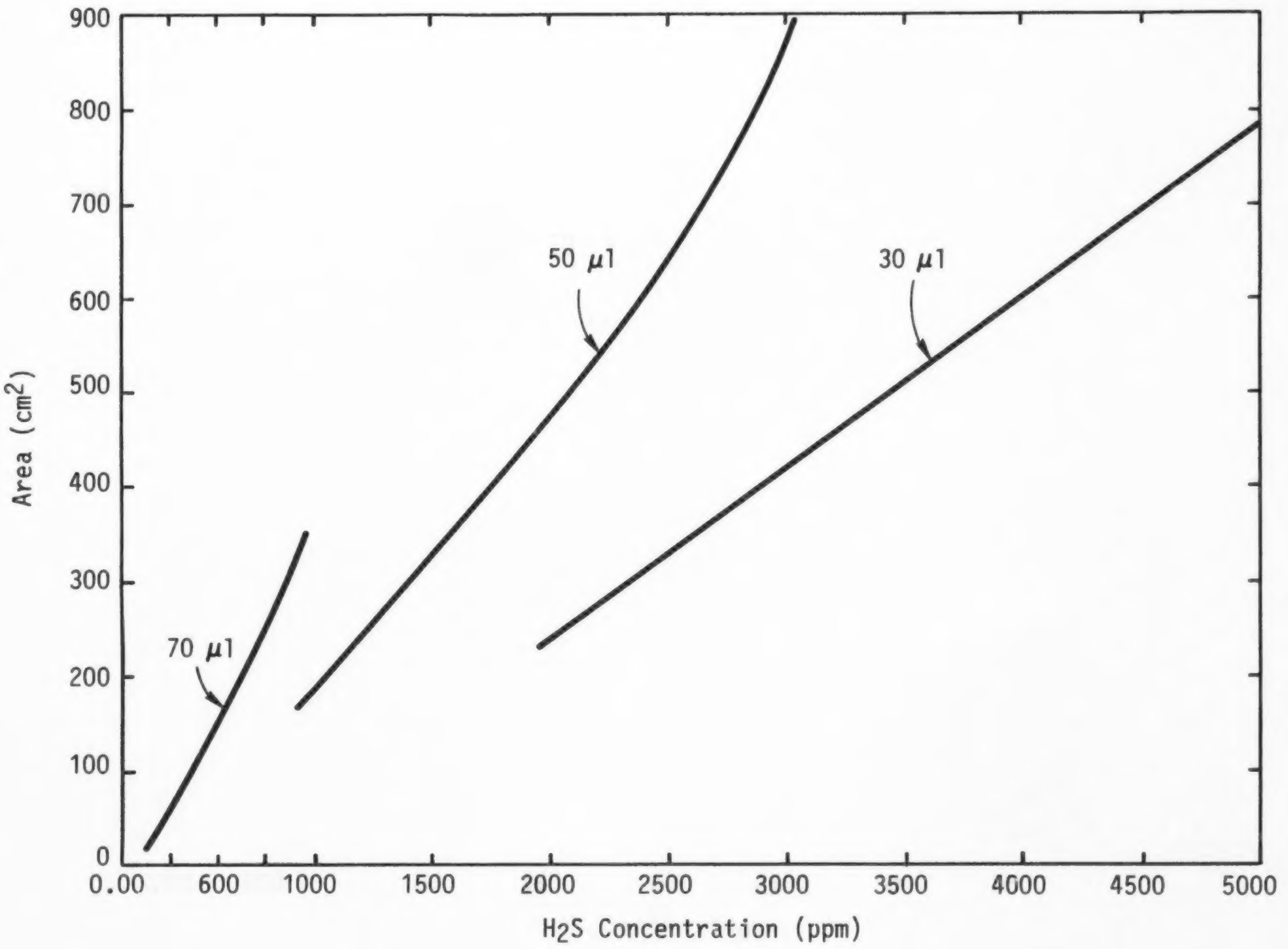


Figure A-11. H_2S calibration curves for 70, 50 and 30 μl syringe injection (5/86).

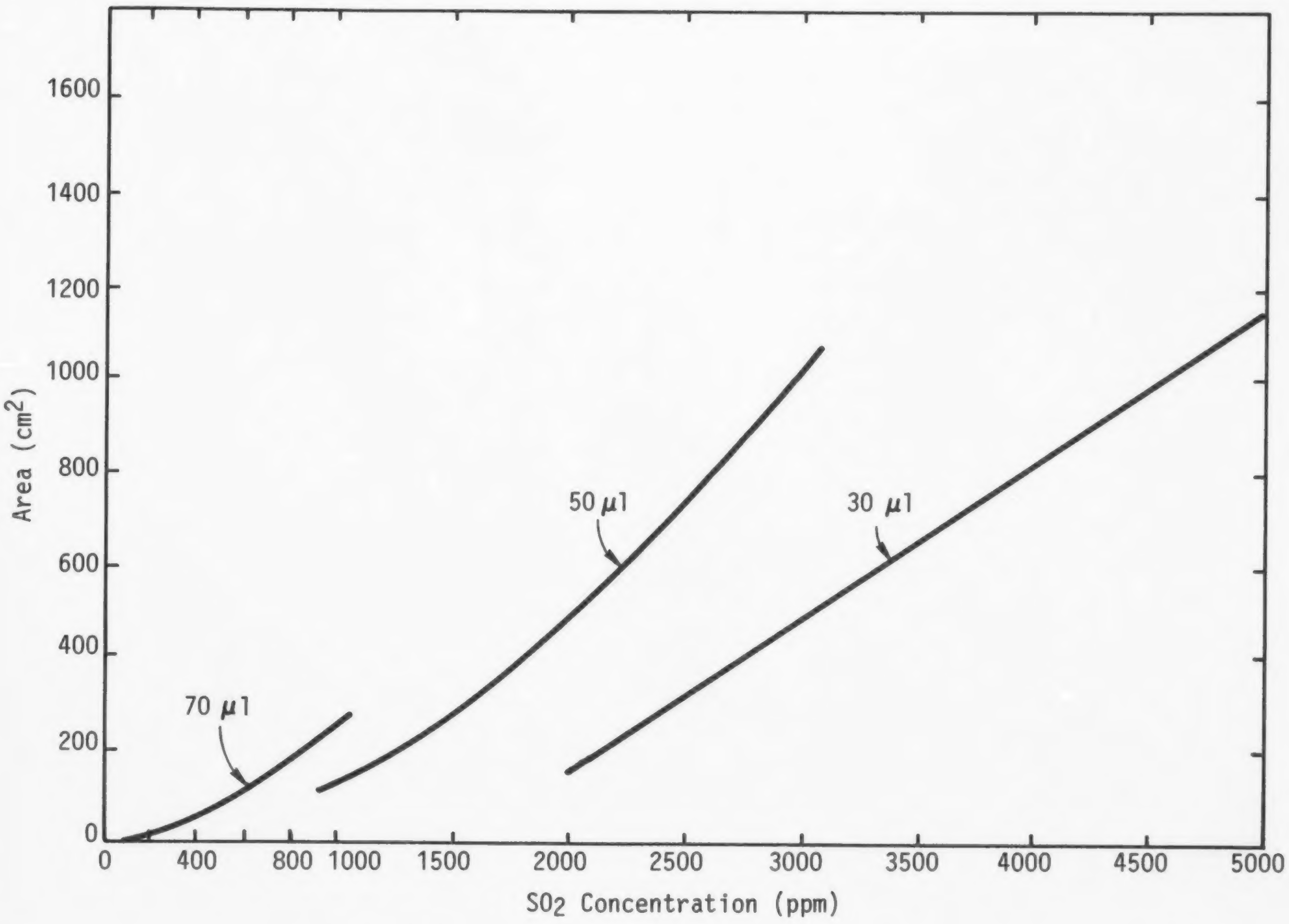


Figure A-12. SO_2 calibration curves for 70, 50 and 30 µl syringe injection (5/86).

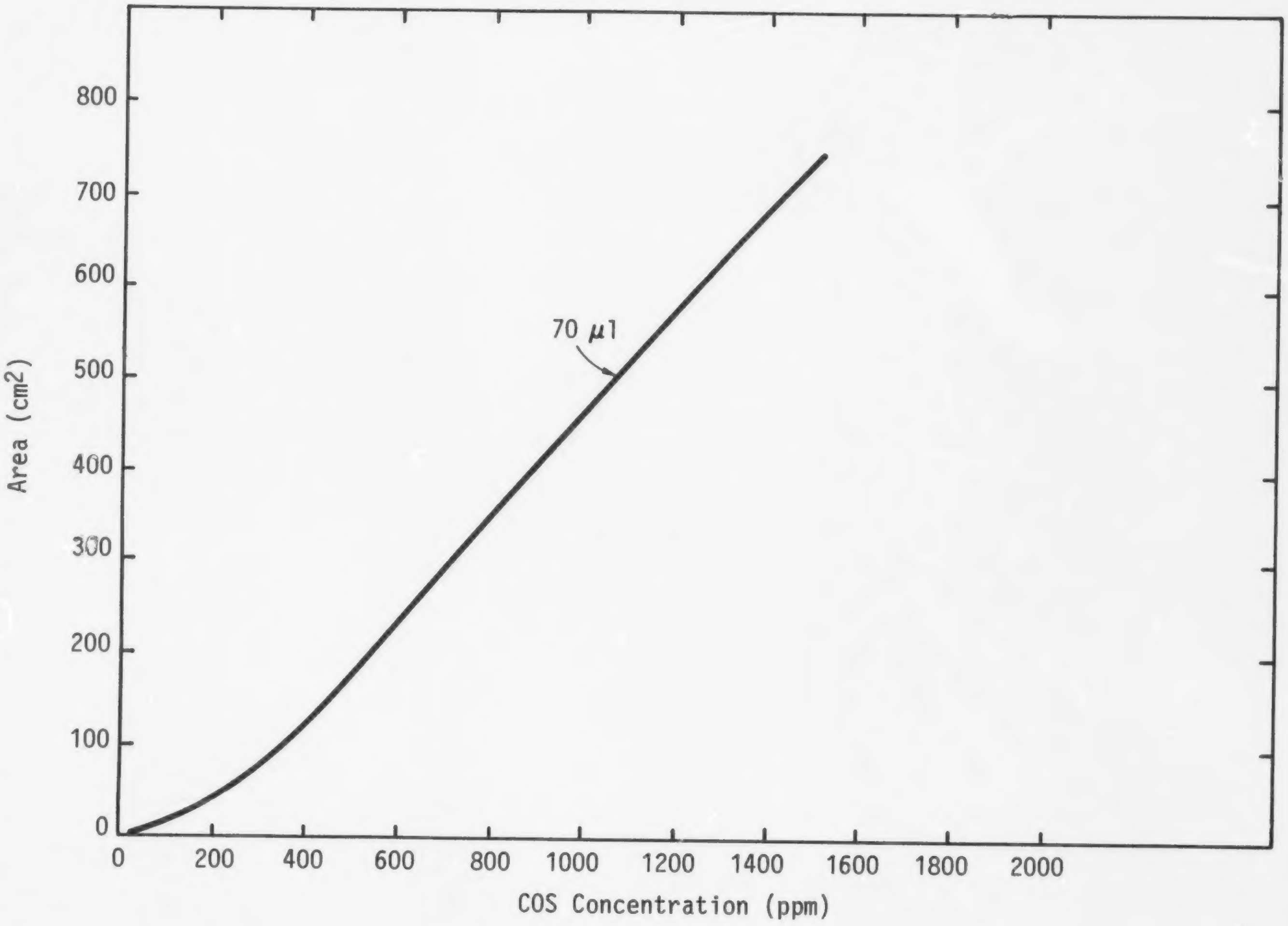


Figure A-13. COS calibration curve for 70 μl syringe injection (5/86).

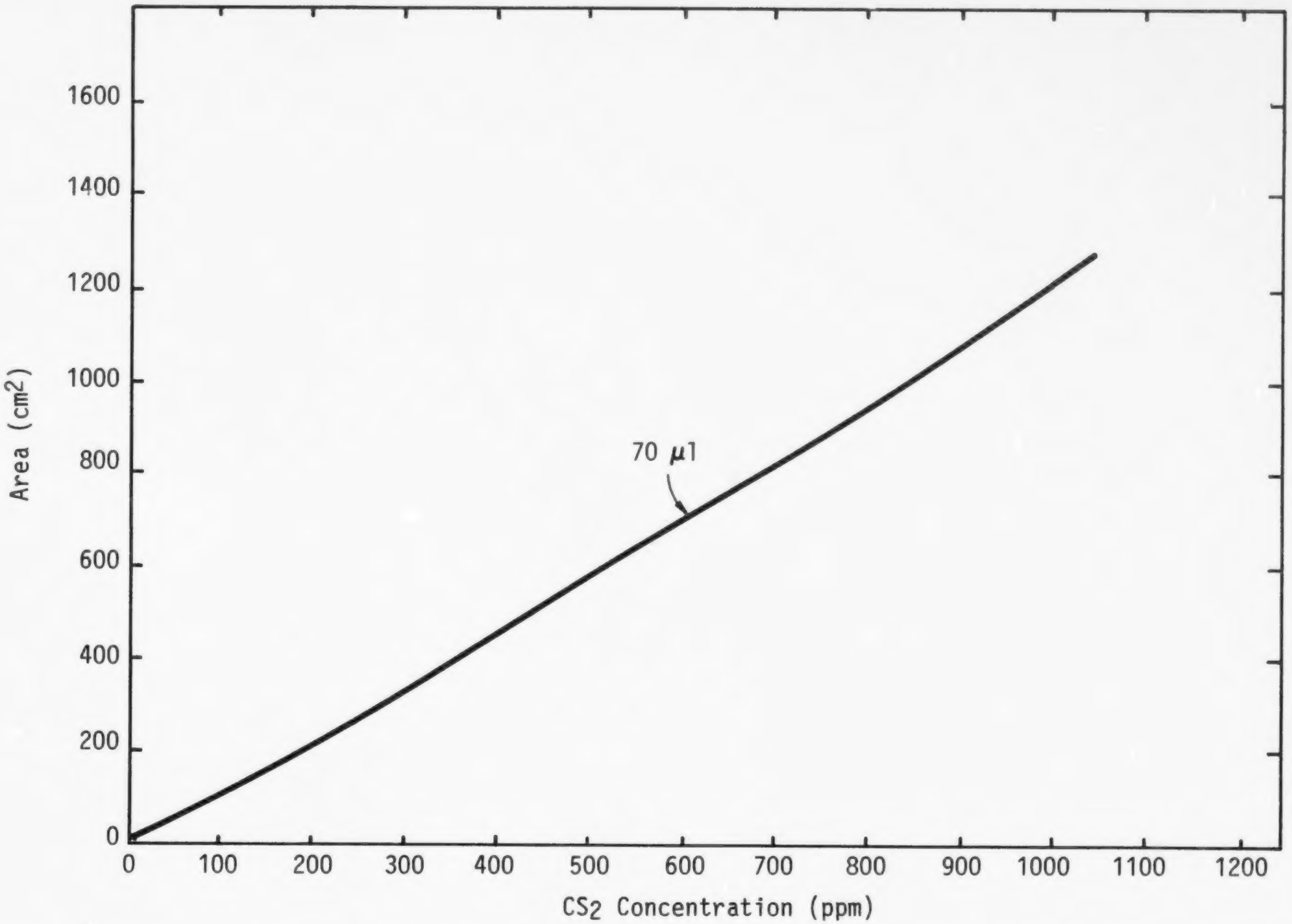


Figure A-14. CS_2 calibration curve for 70 μl syringe injection (5/86).

RUN 262 SULFUR SAMPLES

SENSITIVITIES 50 4

117515
50 ng @ S

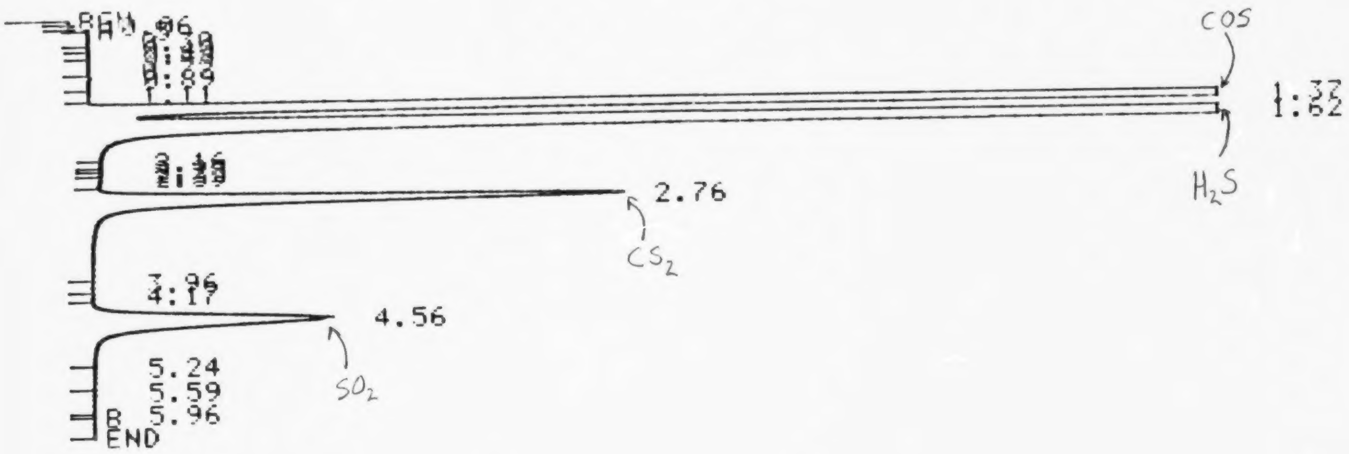


Figure A-15. Gas chromatograph printout example.

```
INST  1  METH   10  FILE   29

RUN    271  SULFUR SAMPLES

SENSITIVITIES    50   4
```

117517
70 ul attn @7

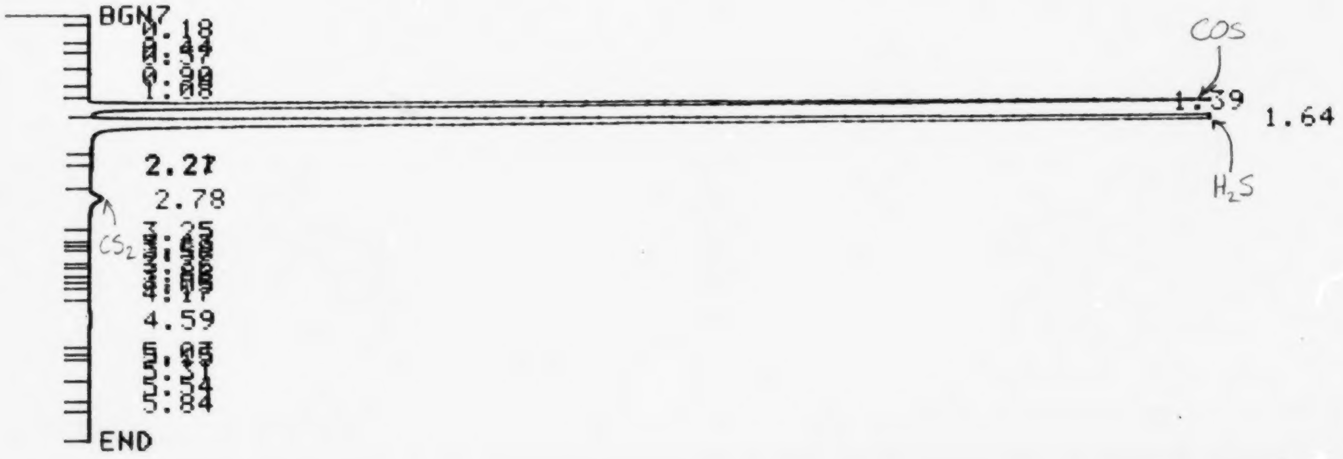
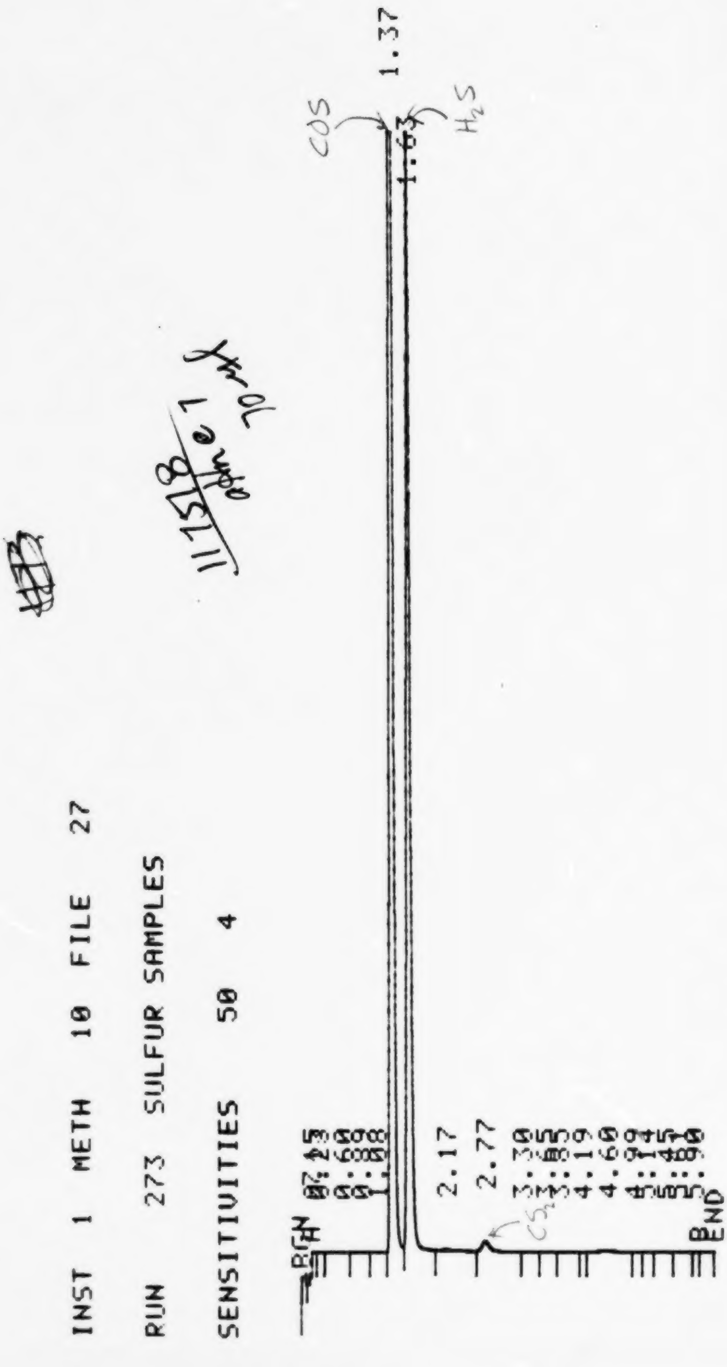


Figure A-16. Gas chromatograph printout example.



INST 1 METH 10 FILE 27

RUN 273 SULFUR SAMPLES

SENSITIVITIES 50 4

Figure A-17. Gas chromatograph printout example.

were not impacted by the clipping of the printed peaks. Identification of the sulfur species associated with each peak was easily achieved.

A.4 Data Reduction

Equations used to calculate results for each of the measurements are discussed below. Many of the results are obtained directly from the measurements and thus do not require calculations. The main results which required calculation for presentation included calcium utilization by capture of sulfur species, sulfur capacity of slags, equilibrium capture of sulfur in slags, and furnace residence time.

A.4.1 Calcium Utilization

The efficiency of the sulfur capture process has been presented in most cases in this program by calculation of the calcium utilization. This has been determined through both gas phase measurements and solids analysis results on the ITR and CTT facilities.

Gas phase determination of the calcium utilization was performed by measurement of the molar change in total sulfur compared to the molar rate of calcium addition:

$$\text{Calcium Utilization}_{(\text{total S})} = \frac{[S]_i - [S]_c}{[S]_T} \cdot \frac{[S]_T}{[Ca]} \times 100\% \qquad \text{(A-6)}$$

where:

$[S]_i$ = the molar sulfur concentration measured before injection of sorbent at location x,

$[S]_c$ = the molar sulfur concentration measured during injection of sorbent at location x,

$[S]_T$ = the equivalent total molar sulfur concentration at location x ($[S]_T = [S]_i$ for gas doping cases, but $[S]_T$ is greater than $[S]_i$ for coal firing if not all the sulfur evolves from the coal),

$[Ca]$ = the equivalent total molar calcium concentration based on the sorbent feed rate.

Nearly all the tests performed in this program were run at a Ca/S molar ratio near 1.0. Higher Ca/S ratios would result in lower calcium utilizations due to reduced sulfur availability.

For cases where coal was fired, not all the sulfur evolved from the coal. In this case, equation A-6 would result in a lower calculated sulfur capture than when only the evolved gas phase sulfur is considered. When based on the gas phase sulfur, the calcium utilization becomes:

$$\text{Calcium Utilization}_{(\text{gas phase S})} = \frac{[S]_i - [S]_c}{[S]_i} \cdot \frac{[S]_i}{[Ca]} \times 100\% \qquad \text{(A-7)}$$

Figures A-18 through A-19 show the difference in sulfur capture results when calculated on these two different bases.

Solid sample determination of calcium utilization is simply the molar ratio of the measured sulfur to calcium:

$$\text{Calcium Utilization} = \frac{S}{MW_S} \cdot \frac{MW_{CaO}}{CaO} \qquad \text{(A-8)}$$

where,

S = weight percent of sulfur in the solid,

CaO = weight percent of calcium oxide in the solid,

MW_S = molecular weight of sulfur, 32,

MW_{CaO} = molecular weight of calcium oxide, 56.

For cases in which coal was fired, a distinction must be made between sulfur bound to char in the solid sample and sulfur which is present as CaS. A calculation procedure was developed to account for the char sulfur by considering the extent of sulfur evolution from a sample without sorbent injection. Equation A-8 can be used with the substitution for the term below of S in determination of the calcium utilization:

$$S_{Ca} = \frac{S_s - [(1 - \frac{SE}{100}) (A_s - CaO) (\frac{S_c}{A_c})]}{[1 - 2.5 (1 - \frac{SE}{100}) (\frac{S_c}{A_c})]} \tag{A-9}$$

where,

A_c = wt % ash in the original coal,

A_s = wt % ash in the sample reported by 240 B analysis, which includes coal ash, CaO and $CaSO_4$,

CaO = wt % of Ca as CaO in sample,

MW_{CaO} = molecular weight of calcium oxide, 56,

MWs = molecular weight of sulfur, 32,

S_c = wt % sulfur in the original coal,

S_{Ca} = wt % sulfur associated with the calcium in the sample,

S_s = wt % sulfur in the sample,

SE = sulfur evolution based on analysis of a solid sample without sorbent present.

A.4.2 Sulfur Capacity

As presented in Section 7.1, the sulfur capacity is defined as:

$$\text{Sulfur Capacity} = C_s = (S) \left(\frac{P_{O_2}}{P_{S_2}}\right)^{1/2} \tag{A-10}$$

where,

S = weight percent of total sulfur in the slag,
P_{O_2} = partial pressure of oxygen, and
P_{S_2} = partial pressure of sulfur above the slag layer.

P_{O_2} and P_{S_2} are determined by equilibrium calculations using the test condition inlet gas mixture and temperature. The weight percent sulfur was determined by solids analysis after the slag reached equilibrium.

A.4.3 Equilibrium Sulfur Capture by Slag

It was stated earlier that the sulfur capacity can be used to calculate the amount of sulfur capture in an actual coal combustion system. First, the equilibrium partial pressures of oxygen and sulfur are determined for a number of gas phase sulfur concentrations (simulating different amounts of sulfur capture) at a given temperature and combustion stoichiometry. Then, for a given slag mixture (determined by the Ca/S ratio) the corresponding weight percent sulfur is calculated using the experimentally obtained sulfur capacity. A mass balance of sulfur can then be performed to determine the actual percentage of gas phase sulfur that would be removed.

A.4.4 Furnace Residence Time

Residence times are calculated by assuming one-dimensional flow in the furnace. Based on the measured temperatures, the bulk mean residence time of a specified furnace zone (τ_2) was calculated by using the following equation:

$$\tau_2 = \frac{V_2}{\dot{V}} \frac{T_o}{T_{m_2}} \tag{A-11}$$

where:

V_2 = volume of furnace zone 2, ft^3,
$\dot{V}$ = volumetric flow rate of gas, SCFS,

T_o = 293°K,

T_{m_2} = bulk mean gas temperature

= $1/2\ (T_i + T_o)_2$.

T_i and T_o are center line temperatures measured at the inlet and the exit of the specific furnace zone, respectively.

APPENDIX B

EXAMPLES OF RAW DATA

B.1 ITR Data Example

22 August 1985

Fuel Rich Flame Studies.
H_2S Injected Downstream
with commercial Linwood Hydrate

Sample No. 02-22-0885 Lab No. 107057

Distance 47cm

ϕ = 2.0

Sample Time 1.5min @ 0907

Burner Air 80cfh

Primary Air 20cfh

Swirl N_2 2cfh

Transport N_2 6cfh

H_2S 47

CH_4 15.7

Precombustor Temp @ TC-9 1280-1300°C

ITR Temp. 1300°C

Gas Sample Rate 4cfh

Gas Sample pressure 2.0" H_2O

Gas Sample Temp 91°C

Sorbent feed rate 1.35 g/min.

LER

14

LAB SAMPLE
TRACKING REPORT
WORK REQUEST

PROJECT NO.
ENGINEER J. Cole
REMARKS:

CHARGE NO. 85 18-20

SAMPLE* NO.	SAMPLE DESCRIPTION	ANALYSIS REQUIRED	SAMPLE PREPARATION	DATE DELIVERED	DATE COMPLETED	COMMENTS
10705-6	H_2S	GC analysis		22-8-85		
10705-7	↕	↕				
107058						
107059						

PLEASE PUT IN ORDER OF PRIORITY FOR ANALYSIS

SULFUR GAS ANALYSIS

RECIEVING DATE: 22-8-85
ANALYSIS DATE: 23-8-85
FROM: QOLG
ANALYST: M. Talebi

SAMPLE NO.	COS ppm	H_2S ppm	CS_2 ppm	SO_2 ppm
107056	165	4560	1350	150
107057	150	3545	470	≤15
107058	135	4410	1125	700
[illegible]59	205	3755	635	345

SULFUR GAS ANALYSIS BY G.C.
RECEIVING DATE: 8/22/85 ANALYSIS DATE: 8/23/85 FROM: ANALYST: M. TROBI

SAMPLE NO	VOLUME ml	AREA COS	AREA H_2S	AREA CS_2	AREA SO_2	COS PPM	H_2S PPM	CS_2 PPM	SO_2 PPM
107056	2.0	1.2515	149.8419	72.4019	0.1536	167	–	–	149
	0.40	0.2624	24.3136	6.3632	–	–	4559	1352	–
107057	2.0	0.9635	132.6387	17.5302	0.0130	151	–	487	[illegible]
	0.40	0.2092	16.2124	1.2042	–	–	3546	446	
107058	2.0	0.8761	148.5619	60.0448	1.1109	137	–	1118	700
	0.40	0.3503	23.1948	5.0360	0.1011	–	4412	1133	–
107059	2.0	1.5282	136.4582	27.3664	0.5214	204	–	633	343
	0.4	0.2826	18.2892	1.9516	0.0759	–	3757	–	–

B.2 CTT Data Example

6/2/86 CTT Rich Zone

FR = 80000 BTU/Hr
SR_1 = 0.6 SR_2 = 1.25
Backfired = On/On
Burner = Premixed

Configuration = (2, 19)
SO_2 Doping = none
Secondary = 500°F
Fuel = Illinois
Sorbent = Linwood AH

T_{INJ} = 2400°F
T_{INJ} = 2115°F

FRC + LC OK

Test 1 (Illinois, Linwood AH, Port 2)

The coal fed well. The sorbent fed well also. The GC sampling ran smoothly. The first time points 1.6 + 1.7 were run, we were running low on coal, so they were repeated.

The testing was done with everything running OK.

Test 2 (Illinois, Linwood AH, Port 4)

The coal fed well. The sorbent fed well also. The GC samples went smoothly.

Temperatures were taken around Injection location to determine tip temperature.

Data by Mike & Eric

6/2/86 CTT Rich Zone

Pt	O_2	CO_2	SO_2	SO_2 Corrected for N_2 Dilution	SO_2	SO_2	% Capture	Actual Ca/S	Test Conditions
	Corrected No Dilution AS MEAS	As meas	As meas		0% O_2	AVG AS MEAS / AVG 0% O_2		Illinois @ 8000	Linwood AH Inj. @ ?
1-1	4.2 3.8	13.1	2520			2520			Baseline
1-2				#117501			Ca/S = ~~0.[illegible]~~ ~~0.79~~	0.74 0.71	GC@ 15
1-3				#117502		Avg	Ca/S = ~~0.80~~	0.72	GC @ 15 Linwood AH on
1-4				#117503			1.25	1.39	GC@15
1-5				#117504		Ca/S =	~~1.34~~; 1.	~~54~~	GC@ 15 Linwood AH on
						Avg Ca/S =	~~1.44~~		
Lunch 1-6	4.2 3.8	12.5	2393			2443	1.32		Baseline
1-7				#117505			2.32	2.54	GC@ 15
1-8				#117506		Ca/S	= ~~2.56~~	~~2.84~~	GC @ 15 Linwood AH on
						Avg	Ca/S =	~~2.69~~	
1-9	4.3 3.9	12.9	2498				2.43		Baseline
								Illinois @80000	Linwood AH @ 4 SR1 = 0.6
2-1	4.4 3.9	13.0	2508			2508			Baseline
2-2				#117507			0.94	0.95	GC @ 15
2-3				#117508		Ca/S =	~~1.04~~,	~~1.05~~	GC @ 15 Linwood AH on
2-4	5.2	13.8	2699			Avg.	Ca/S =	~~1.05~~	T_2 = 2335°F
2-5	4.9	13.9	2734				0.94		T_{10} = 1975°F

$$T_4\ \text{est} = 2335°F - \left(\frac{360°F}{24\,in}\right)(14.75\,in)$$

(T[illegible])

$$= 2113°F$$

6/12/86 CIT Sorbent Calculations

Test 1(#2 Illinois, Linwood AH, Part 2)

Feeder Setting	Before (g/min)	Ca/S	After (g/min)	Ca/S	% Capture
250	3.10	0.74 ~~0.82~~	2.97	0.71 ~~0.79~~	
455	5.23	1.25 ~~1.39~~	5.80	1.39 ~~1.84~~	
780	9.38	2.32 ~~2.56~~	10.3	2.54 ~~2.81~~	
Test 2 312	3.92	0.94 ~~1.04~~	3.93	0.95 ~~1.05~~	

Feeder @ 250

$\mathring{M} = \frac{2.82}{\cancel{2.55}}$

SO_2: 2520

wt% Ca = 51.6

feedrate needed for Ca/S = 1.0: $\frac{2.82}{\cancel{2.55}}(2520)(\frac{1}{51.6})(0.0303005)$

= ~~3.77~~ g/min 4.17

Feeder @ 455

$SO_2 = 2520$

feedrate needed = ~~3.77~~ g/min 4.17

Feeder @ 780

$SO_2 = 2443$

feedrate needed = ~~3.66~~ g/min 4.05

Feeder @ 312

$SO_2 = 2508$

feedrate needed = ~~3.75~~ g/min 4.15

6-2-86 FEEDER CALIBRATION MATERIAL LINWOOD AH #

DATE	RUN#	TARE M_1	GROSS M_2	NET M_3	TIME(MIN)	FEED RATE	COMMENTS
6/2 -	1	32.58	45	12.42	4	3.10g/min	Before 250 3/8" screw 80.64
"	1	32.58	41.5	8.92	3	2.97g/min	After 250 3/8" screw 84.17
"	2	32.58	53.5	20.92	4	5.23g/min	Before 455 3/8" screw 86.99
"	2	32.58	50	~~77.58~~ 17.42	3	5.8g/min	After ~~After~~ 455 3/8" screw 78.44
"	3	32.58	72.4	3982	4	9.95g/min	Before 709 3/8" screw 70.75
	3	32.58	57.4	~~14.42~~ 25.02	3	8.34g/min	After 709 3/8" screw

~~6/2/86~~ FEEDER CALIBR TION MATERIAL [illegible] J#

DATE	RUN#	TARE M_1	GROSS M_2	NET M_3	TIME (Min)	FEED RATE	COMMENTS
4/2	4	32.0	63.2	31.2	4	7.8 g/min	Before 660 3/4" screw
"	4	32	60.5	28.5	4	7.25 g/min	Before 720 3/8" screw
"	4	32	50.75	18.75	4 2	9.38 g/min	Before 780 3/4" screw 53.16
"	4	32	63.0	31	3	10.3 g/min	After 780 3/8" screw 25.72
"	5	32	47.7	15.7	4	3.92 g/min	Before 312 3/8" screw 71.59
"	5	32	43.8	11.8	3	3.73 g/min	After 312 3/8" screw 71.38

Date: 6/2/86

Conditions: Illinois FR=80000 BTU/Hr SR_1 = 0.6
Linwood AH T_{INJ} = 2400°F (Port 2)

Sample # (other)	COS	H_2S	CS_2	SO_2	Total	Ca/S	Gas Phase % Cap	Gas Phase % Cap. Based on Ca/S=1.0
Port 15 117501	1131	2820	25	60	4036			
Port 15 117502	341	1710	10	80	2141	0.72 ~~280~~	47.0	
Port 15 117503	1197	2610	23	280	4110			
Port 15 117504	146	577	10	80	813	1.32 ~~1.46~~	80.2	
Port 15 117505	821	2480	24	210	3535			
Port 15 117506	120	490	10	60	680	2.43 ~~2.69~~	80.8	

Date: 6/2/86

Conditions: Illinois FR = 80000 BTU/Hr SR$_1$ = 0.6
Linwood AH T_{INJ} = 2115°F (Port 4)

Sample # (other)	COS	H_2S	CS_2	SO_2	Total	Ca/S	Gas Phase % Cap	Gas phase % Cap. Based on Ca/S=1.0
Port 15 117507	801	3230	23	120	4174			
Port 15 117508	317	1175	7	60	1559	0.94 ~~1.05~~	62.6	66.6

LAB SAMPLE
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367

NOTE
NOTICE CHANGES
IN SOME
G.C. RESULTS
T. Grogan

PROJECT NO. 8518-20 CHARGE NO.________
ENGINEER E. Moller
REMARKS:________

SAMPLE* NO.	SAMPLE DESCRIPTION	ANALYSIS REQUIRED	SAMPLE PREPARATION	DATE DELIVERED	DATE COMPLETED	COMMENTS
	Conditions for following Samples Illinois, SR.=0.6, FR=80000 BTU/hr					
	Inj @ 2, N_2 on					
108357	Sample @ 1c	GC ✓	none	5/29/86	5/29/86	
108358	Sample @ 4	" ✓	"	"	"	
108359	Sample @ 9	" ✓	"	"	"	
108360	Sample @ 15	" ✓	"	"	"	
108361	Linwood AH on Sample @ 15	" ✓	"	"	"	
108362	Linwood AH on Sample @ 9	" ✓	"	"	"	
108363	Linwood AH on Sample @ 4	" ✓	"	"	"	
108364	Solid Sample @ 15	Cl, S, 2403 / ASTM/ASH	Dry	5/29/86	6/9/86	

* PLEASE PUT IN ORDER OF PRIORITY FOR ANALYSIS

ULTIMATE ANALYSIS

ject No: 8518-20

Project Sample No:

Lab Sample No:

Date Received: 5129186

Sample Description: Solid Coal Sample

Date of Analysis: 612-619

Analyzed By: J. McInerney

Sample Preparation: Dried 2 hrs at @ 100°C

% By Weight

	Dry				Dry				Dry				Analytical Method *
Analysis No.	108364												
Carbon	56.98												
Hydrogen	0.54												
Oxygen													
Nitrogen	0.47												
Sulfur	5.64 6.14	> 5.89											
Ash 240B	41.58												
Ash ASTM	55.32												
Moisture													
Total													

Comments: CaO Analysis Results:

108364 - 17.48% CaO 12.49%Ca

*Unless otherwise specified, analytical methods are as follows:

Carbon, Hydrogen, Nitrogen, Ash: Perkin Elmer Model 240 Elemental Analyzer.

Sulfur: Leco Model SC 32 Sulfur Analyzer.

Moisture: ASTM Method D-3173

Oxygen: Difference

ER

LAB SAMPLE
TRACKING REPORT
WORK REQUEST

Note 376 CHANGES IN SOME G.C RESULTS T. Grossman

PROJECT NO. 8518-20 CHARGE NO. ________

ENGINEER E Moller

REMARKS: ________

SAMPLE* NO.	SAMPLE DESCRIPTION	ANALYSIS REQUIRED	SAMPLE PREPARATION	DATE DELIVERED	DATE COMPLETED	COMMENTS
Conditions	Illinois, Inj. @ 2	FR = 80000 BTU/Hr Linwood AH	SR = 0.6			
117501	GC Sample @ 15	GC ✓	None	6/2/86	6/2/86	
117502	GC Sample @ 15 Linwood AH @ C/S =	" ✓	"	"	"	
117503	GC Sample @ 15	" ✓	"	"	"	
117504	GC Sample @ 15 Linwood AH @ C/S =	" ✓	"	"	"	
117505	GC Sample @ 15	" ✓	"	"	"	
117506	GC Sample @ 15 Linwood AH @ C/S =	" ✓	"	"	"	
	Illinois FR = 80 K Inj. @ 4	SR = 0.6 Linwood AH				
507	GC Sample @ 15	✓	GC	6/2/86	"	
117508	GC Sample @ 15 C/S = 1.0 Linwood AH	" ✓	"	"	"	

* PLEASE PUT IN ORDER OF PRIORITY FOR ANALYSIS

STANDARD CHECKS

DATE	GAS	STD. CONC. (ppm)	RETENTION TIME (min)	ATTN.	INJECTION VOL. (μl)	AREA (cm²)	CONC. (ppm) DETERMINED
6/2/86	SO_2	1800	4.63	9	50	404.6643	1830
BEGINNING OF DAY	SO_2	1800	4.65	9	50	406.9785	1830
	SO_2	1800	4.67	9	50	410.6036	1840
	SO_2	1800	4.67	9	50	425.4515	1070
	SO_2	1800	4.69	9	50	424.5504	1[illegible]10
	SO_2	1800	4.67	9	50	382.2796	1770
6/2/86	SO_2	1800	4.69	9	50	417.2800	18[illegible]
END OF DAY	SO_2	1800	4.72	9	50	387.2358	17[illegible]
	SO_2	1800	4.70	9	50	384.8601	1780
	SO_2	1800	4.72	9	50	402.2272	1[illegible]0

Mouer's Sulfur Samples

Date	Sample No.	Injection Vol. (μl)	Retention Time (min)	Area (cm²)	Gas Species	Conc. (ppm)	Avg. of Closest 2
6/2/86	117501	70	1.43	554.2912	COS	1127 ~~>1000~~	1131
			1.70	1027.0220	H_2S	—	2820
			2.87	25.0240	CS_2	25	25
			4.70	1.1847	SO_2	~~<100~~ 60	60
	117501	70	1.45	530.1043	COS	1095 >1000	
			1.69	1027.5635	H_2S	—	
			2.88	23.8758	CS_2	24	
			4.71	0.7931	SO_2	~~<100~~ <60	
	117501	70	1.44	561.1724	COS	1130 ~~>1000~~	
			1.71	1071.0220	H_2S	—	
			2.88	26.0288	CS_2	25	
			4.69	0.4210	SO_2	~~<100~~ <60	
	117501	50	1.44	353.4028	COS	—	
			1.69	773.1609	H_2S	2790	
			2.88	13.0841	CS_2	—	
			4.71	0.2877	SO_2	—	
	117501	50	1.44	339.9270	COS	—	
			1.69	747.5609	H_2S	2720	
			2.88	12.3187	CS_2	—	
			4.70	0.2551	SO_2	—	
	117501	50	1.44	366.9196	COS	—	
			1.69	808.7961	H_2S	2050	
			2.88	13.6217	CS_2	—	
			4.74	0.2270	SO_2	—	
6/2/86	117502	70	1.45	104.1254	COS	345	341
			1.71	632.2380	H_2S	—	1710
			2.89	3.6920	CS_2	—	10
			4.75	0.1431	SO_2	— <60	80
	117502	70	1.45	99.7068	COS	337	
			1.70	619.2947	H_2S	—	
			2.88	3.4603	CS_2	<10	
			4.73	0.1475	SO_2	<100	
	117502	50	1.44	53.8854	COS	—	
			1.69	387.7478	H_2S	1690	
			2.88	1.9306	CS_2	<10	
			4.74	0.0729	SO_2	0	

Moler's Sulfur Samples

Date	Sample No.	Injection Vol. (ml)	Retention Time (min)	Area (cm²)	Gas Species	Conc. (ppm)	
6/2/86	117502	50	1.44	51.0182	COS	—	
			1.70	365.1174	H_2S	1605	
			2.88	1.7992	CS_2	—	
			4.74	0.0884	SO_2	—	
	117502	50	1.44	55.4470	COS	—	
			1.70	401.5513	H_2S	1720	
			2.89	1.9478	CS_2	—	
			4.73	0.0436	SO_2	—	
6/2/86	117503	70	1.44	528.9574	COS	~~≥1000~~ 1197	1197
			1.69	944.9472	H_2S	—	2610
			2.88	18.2976	CS_2	10	23
			4.74	15.7177	SO_2	240	280
	117503	70	1.44	577.8432	COS	~~≥1000~~ 1197	
			1.69	1018.5932	H_2S	—	
			2.88	21.8419	CS_2	23	
			4.74	20.8358	SO_2	270	
	117503	70	1.44	578.9900	COS	~~≥1000~~ 1197	
			1.71	1019.3715	H_2S	—	
			2.88	21.6563	CS_2	23	
			4.75	24.4864	SO_2	290	
	117503	50	1.44	370.0736	COS	—	
			1.70	707.9526	H_2S	2640	
			2.89	11.2832	CS_2	—	
			4.75	13.2166	SO_2	—	
	117503	50	1.44	355.9219	COS	—	
			1.70	684.1139	H_2S	2580	
			2.89	10.4547	CS_2	—	
			4.75	12.1964	SO_2	—	
	117503	50	1.44	385.2492	COS		
			1.69	739.5328	H_2S	2726	
			2.89	11.9206	CS_2	—	
			4.76	15.1929	SO_2	—	
6/2/86	117504	70	1.44	22.4166	COS	145	146
			1.70	146.5292	H_2S	[illegible] 585	577
			2.89	0.7466	CS_2	<10	10
			4.77	0.3187	SO_2	<100	80

MOWER'S SULFUR SAMPLES

DATE	SAMPLE No.	INJECTION VOL. (µl)	RETENTION TIME (min)	AREA (cm²)	GAS SPECIES	CONC. (ppm)	
6/2/86	117504	70	1.45	20.2150	COS	147	
			1.71	139.8374	H_2S	570	
			2.90	0.6484	CS_2	<10	
			4.78	0.1418	SO_2	~~[illegible]~~ <60	
	117504	70	1.46	17.8169	COS	127	
			1.72	121.8764	H_2S	535	
			2.91	0.5486	CS_2	<10	
			4.80	0.0955	SO_2	~~[illegible]~~ 0	
6/2/86	117505	70	1.44	363.0080	COS	827	821
			1.70	905.4208	H_2S	—	2480
			2.89	21.5795	CS_2	21	24
			4.78	7.1724	SO_2	140	210
	117505	70	1.45	378.2451	COS	835	
			1.71	943.4726	H_2S	—	
			2.90	23.5788	CS_2	24	
			4.78	10.7648	SO_2	210	
	117505	70	1.45	406.3641	COS	856	
			1.71	990.9452	H_2S	—	
			2.90	20.1107	CS_2	25	
			4.79	11.5513	SO_2	210	
	117505	50	1.45	235.6428	COS	—	
			1.71	660.6438	H_2S	2510	
			2.90	13.4131	CS_2	—	
			4.79	6.4153	SO_2	—	
	117505	50	1.44	222.9145	COS	—	
			1.69	631.9308	H_2S	[illegible] 2450	
			2.88	12.3980	CS_2	—	
			4.77	5.6425	SO_2	—	
	117505	50	1.46	251.5148	COS	—	
			1.72	709.0585	H_2S	[illegible] 2645	
			2.91	13.8323	CS_2	—	
			4.80	6.3740	SO_2		
6/2/86	117506	70	1.49	15.4848	COS	130	120
			1.76	100.8230	H_2S	490	490
			2.99	0.5557	CS_2	<10	10
			4.96	0.2014	SO_2	<60	60

Mouer's Sulfur Samples

DATE	SAMPLE No.	INJECTION VOL. (µl)	RETENTION TIME (min)	AREA (cm²)	GAS SPECIES	CONC. (ppm)	
6/2/86	117506	70	1.36	15.2844	COS	120	
			1.61	102.7379	H_2S	1190	
			2.74	0.4933	CS_2	<10	
			4.53	0.1357	SO_2	~~≤100~~ <60	
	117506	70	1.40	14.9612	COS	120	
			1.66	103.8438	H_2S	500	
			2.81	0.4411	CS_2	<10	
			4.67	0.1228	SO_2	~~≤100~~ <60	
6/2/86	117507	70	1.41	342.4960	COS	807	801
			1.68	1129.2081	H_2S	—	3230
			2.82	22.9926	CS_2	23	23
			4.67	3.3724	SO_2	~100	120
	117507	70	1.40	356.3724	COS	796	
			1.63	1116.6105	H_2S	—	
			2.81	23.8579	CS_2	24	
			4.67	5.9449	SO_2	140	
	117507	50	1.40	221.9008	COS	—	
			1.66	895.8771	H_2S	2275	
			2.82	13.5360	CS_2	—	
			4.68	3.2766	SO_2	—	
	117507	50	1.40	228.8640	COS	—	
			1.66	920.3712	H_2S	—	
			2.82	13.9545	CS_2	—	
			4.68	3.4516	SO_2	—	
	117507	30	1.42	85.8982	COS	—	
			1.68	469.2787	H_2S	[illegible]	
			2.83	5.0019	CS_2	—	
			4.71	1.4599	SO_2	—	
	117507	30	1.40	84.5004	COS	—	
			1.65	465.2032	H_2S	[illegible]	
			2.82	4.8995	CS_2	—	
			4.67	1.0973	SO_2	—	
6/2/86	117508	70	1.39	92.5542	COS	320	317
			1.65	447.0988	H_2S		1175
			2.81	7.3078	CS_2	7	7
			4.67	0.6027	SO_2	<60	60

UEE'S SULFUR SAMPLES

DATE	SAMPLE No.	INJECTION VOL. (µl)	RETENTION TIME (min)	AREA (cm²)	GAS SPECIES	CONC. (ppm)	
11/2/86	117508	70	1.42	89.5846	COS	315	
			1.67	436.6336	H_2S	—	
			2.84	7.1753	CS_2	7	
			4.72	0.5176	SO_2	~~400~~ 45	
	117508	50	1.40	44.9715	COS	—	
			1.66	236.1958	H_2S	1170	
			2.82	3.5718	CS_2	—	
			4.70	0.2528	SO_2	—	
	117508	50	1.41	45.6857	COS	—	
			1.67	239.4624	H_2S	1100	
			2.83	3.4857	CS_2	—	
			4.72	0.2772	SO_2	—	

B.3 HTO Data Example

Dec. 17, '85

7:45: * Checking the flowrates.

* Changing bottle (CO) — CO bottle leaking.

* Reducing data for Tim.

} • (15 min. lunch)

* Reducing data of G. C. for Tim

* Scrubbing samples from the boats.

5:10 * Checking the system.

Dec. 18, '85

7:50 * checking the system

* Checking N2 (another one)
CO (another one)

* Washing Boats.

* Grinding samples. (for total sulfur measure

* Preparing ash sample for tonight-run.

* Preparing ash sample for Tim.
before putting into oven.

* Reviewing monthly reports.

12:00
~ (lunch time)
12:45

* Preparing bottles for 6:00 P.M.

* Preparing writing short notes for results.

* SR=0.5, T=1400°c t0

ⓐⓑ 1

ⓐ Ca/S=1 , 5%, B_2O_3, (CaO)

ⓑ " , 5%, CaF_2, (CaO)

ⓒⓓ 2

ⓒ " , 5%, Fe_2O_3, (CaO)

ⓓ " , 5%, P_2O_5, (CaO)

ⓐ Transparent, Brown, ~~a~~ molten slag with smooth surface. Two small pieces are non-transparent.

ⓑ Transparent, light brown, molten slag with semi-smooth surface. Some "unmolten" staff in the sl

ⓒ Transparent, dark brown, molten slag with smooth surface.

ⓓ Transparent, very light yellow, molten slag with ~~Some~~ Some bobbles in the slag. Smooth surfaces.

SR=0.5, T=1400°C, 10 Min Desulfur

1 ⓐⓑ

2 ⓒⓓ

ⓐ Ca/S=1(CaS), 10% B_2O_3

ⓑ Ca/S=1(CaS), 10% Fe_2O_3

ⓒ Ca/S=2(CaS), 10% B_2O_3

ⓓ Ca/S=1(CaS).

230A

221A

ⓑ → Slags crept out of the boat

ⓐ Partially molten slag. (Black). Smooth surface on some of the slag.

ⓑ Porous, black slag (Partially molten) with rough surface. A thin layer was found.

ⓒ porous, shrinked, partially-molten slag. (block)
With rough surfaces. No strong rxn with Pt.

ⓓ Same as ⓒ

Go Home 6:30 P.M.

Dec. 19, '85

7:45 * Grinding samples for total sulfur
* Checking the system.
* Washing the boats.
* Finding CO or Purchasing CO.
* Tabulate old desulfurization data.

(1 HR Lunch)

5:00 Go Home.

Dec. 20, '85

* 7:30 → in the Mason Office.
1 HR for Baki's project.
* Checking the system
* Reducing data for Tim (G.C.)
* Change CO bottle
* Check VBA cryogenics
* Preparing taking out boats.
* Taking out the boats

/R

LAB SAMPLE
TRACKING REPORT
WORK REQUEST

PROJECT NO.:
CHARGE NO. 8518-20
ENGINEER Bruce Li
REMARKS:

SR=0.5 T=1400°C

SAMPLE* NO.	SAMPLE DESCRIPTION	ANALYSIS REQUIRED	SAMPLE PREPARATION	DATE DELIVERED	DATE COMPLETED	COMMENTS
108759	Ca/S=1, CaS, 10% B_2O_3, 1HR	Total Sulfur (~1%)	PULVERIZED & DRIED FOR 1½HR @ 105C	12/17/85	12/19/85	%S = 0.20, 0.14
108760	Ca/S=1, CaS 10% Fe_2O_3, 1 HR	" (~1%)	"	"	"	%S = 0.84
108761	Ca/S=2, CaS 10% B_2O_3, 1HR	" (~5%)	"	"	"	%S = 2.77
108762	Ca/S=1, CaS, 1HR	" (~1%)	"	"	"	%S = 0.48
108763	Ca/S=1, CaS 10% B_2O_3, 30min	" (~5%)	"	"	"	%S = 1.28, 1.28
108764	Ca/S=1, CaS 10% Fe_2O_3, 30min	" (~5%)	"	"	"	%S = 17.5
08752	Ca/S=2, CaS 10% B_2O_3, 30min	" ? (~20%)	"	"	"	%S = 9.30
08754	Ca/S=1, CaS 30min	" (~5%)	"	"	"	%S = 4.98
108755	Ca/S=1, CaS 10% B_2O_3, 10min	" (~10%)	"	"	"	%S = 0.19, 0.10
08756	Ca/S=1, CaS 10% Fe_2O_3, 10min	" (~10%)	"	"	"	%S = 2.02
08757	Ca/S=2, CaS 10% B_2O_3, 10min	" ?(~20%)	"	"	"	%S = 4.90
08758	Ca/S=1, CaS, 10min	" (~10%)	"	"	"	%S = 2.66

Not Good Data!

* PLEASE PUT IN ORDER OF PRIORITY FOR ANALYSIS

LAB SAMPLE
TRACKING REPORT
WORK REQUEST

PROJECT NO.__________ CHARGE NO. 8518-20
ENGINEER Bruce Lai
REMARKS: If amounts of sample are not enough, please let me know.

SAMPLE* NO.	SAMPLE DESCRIPTION	ANALYSIS REQUIRED	SAMPLE PREPARATION	DATE DELIVERED	DATE COMPLETED	COMMENTS
108765	Ca/S=1, CaS 10% B_2O_3, 0 Min	Total Sulfur (~21%)	PULVERIZED & DRIED FOR 1½ HRS. @ 105°C	12/18/'85	12/19/85	%S = 17.7
108766	Ca/S=1, CaS 10% Fe_2O_3, 0 Min	" (~21%)	"	"	"	%S = 17.8
108767	Ca/S=1, CaS 10% B_2O_3, 0 Min	" (~21%)	"	"	"	%S = 24.3
108768	Ca/S=1, CaS, 0 Min	" (~21%)	"	"	"	%S = 18.5, 18.8

* PLEASE PUT IN ORDER OF PRIORITY FOR ANALYSIS

LAB SAMPLE
TRACKING REPORT
WORK REQUEST

PROJECT NO.
CHARGE NO. 8518-20
ENGINEER Bruce Li
REMARKS:

SR=0.5, T=1400°C

SAMPLE* NO.	SAMPLE DESCRIPTION	ANALYSIS REQUIRED	SAMPLE PREPARATION	DATE DELIVERED	DATE COMPLETED	COMMENTS
08769	Ca/S=2, CaO, 10% B_2O_3, 48HR	Total Sulfur (~5%)	PULVERIZED & DRIED FOR 2 HRS. @ 106°C	12/19/'85	12/19/85	%S = 1.39
08770	Ca/S=1, CaO 10% CaF_2, 48HR	" (~1%)	"	"	"	%S = 0.37, 0.25
08771	Ca/S=1, CaO 48HR	" (~1%)	"	"	"	%S = 0.42
08772	Ca/S=1, CaS 10% B_2O_3, 10 min	" (~10%)	"	"	"	%S = 3.86
08773	Ca/S=1, CaS 10% Fe_2O_3, 10 min	" (~10%)	"	"	"	%S = 8.46
08774	Ca/S=2, CaS 10% B_2O_3, 10 min	? " (~ 20%)	"	"	"	%S = 15.8, 16.0
08775	Ca/S=1, CaS 10 min	(~10%)	"	"	"	%S = 11.6, 12.2

* PLEASE PUT IN ORDER OF PRIORITY FOR ANALYSIS

Desulfurization Data

P_1

Sample #	Temperature (°C)	S.R.		Running Time	Ca/S		Wt% S	$\log\frac{(Wt\%S)}{(Wt\%S)_{0}}$	Melted?
108514	—	—		0 min.	1(CaS only)		42.7 %	—	—
108470	1400°C	0.5		12 min	"		41.65%	-0.011	No.
108473	"	"		30 min	"		42.15%	-0.006	No.
108476	"	"		60 min	"		42.55%	-0.002	No.
108513	—	—		0 min	1. (CaS + Ash) Well Mixed		21.6 %	—	—
108471	1400°C	0.5		12 min	"		11.35%	-0.28	Partially molten.
108474	"	"		30 min	"		6.07%	-0.55	Partially molten.
108479	"	"		60 min	"		0.94%	-1.36	Yes.

P_2

Sample #	Temperature (°C)	S.R.		Running Time	Ca/S		wt-% S	$\log \frac{[S\%]}{[S\%]_{initial}}$	Melted?
108497	1400°C	0.5		0 min	0.5 (CaS+Ash)		13.75%	—	—
108498	"	"		12 min	"		3.28%	-0.62	Yes.
108499	"	"		30 min	"		1.14%	-1.08	Yes.
108500	"	"		60 min	"		1.05%	-1.12	Yes.
108501	1400°C	0.5		0 min	2.0 (CaS+Ash)		25.9%	—	—
108502	"	"		12 min	"		22.8%	-0.06	No.
108503	"	"		30 min	"		19.5%	-0.12	No.
108504	"	"		60 min	"		17.5%	-0.17	No.

Sample #	Temperature (°C)	S.R.		Running Time	Ca/S		Wt% S	$\log\frac{(Wt\%S)}{(Wt\%S)_{t=0}}$	Melted.
108472	1400°C	0.5		12 min.	1. (CaS + Ash As Two Layers)		15.%	-0.16	Partially Melted
108475	"	"		30 min.	"		9.27%	-0.37	Partially Melted
108480	"	"		60 min.	"		6.02%	-0.55	Yes.
108768	1400°C	0.5		0 min	1. (CaS + Ash Well Mixed)		18.7%	—	—
108775	"	"		12 min	"		11.9%	-0.20	Partially molten.
108754	"	"		30 min	"		4.98%	-0.57	Partially molten.
108762	"	"		60 min	"		0.48%	-1.59	Yes.
108765	1400°c	0.5		0 min	Ca/S=1 (CaS) 10% B_2O_3		17.7%	—	—

P4

Sample #	Temperature (°C)	S.R.		Running Time	Ca/S		Wt% S	$\log\frac{(Wt\%S)}{(Wt\%S)_{t=0}}$	Melted!
108772	1400°C	0.5		12 min.	Ca/S=1 (CaS) 10% B_2O_3		3.86%	-0.66	Partially Molten.
108763	"	"		30 min	"		1.28%	-1.14	Yes.
108759	"	"		60 min	"		0.17%	-2.02	Yes.
108766	1400°C	0.5		0 min	Ca/S=1 (CaS) 10% Fe_2O_3		17.8%	—	—
108773	"	"		12 min	"		8.46%	-0.32	Partially Molten
108764	"	"		30 min	"		17.5%		Yes.
108760	"	"		60 min	"		0.84%	-1.33	Yes.
108767	1400°C	0.5		0 min.	Ca/S=2 (CaS) 10% B_2O_3		24.3%	—	—

Sample #	Temperature (°C)	S.R.		Running Time	Ca/S		Wt% S	$\log \frac{(Wt\%S)}{(Wt\%S)_{200}}$	Melted
P_F 108774	1400°C	0.5		12 min	Ca/S=2 (CaS) 10% B_2O_3		15.9%	-0.18	Not Melted
108752	"	"		30 min	"		9.3%	-0.42	Partially Melted
108761	"	"		60 min	"		2.77%	-0.94	Yes.

~~Ex:~~ Table X.

Sample #	Temperature (°C)	S.R.	$\left(\frac{P_{O_2}}{P_{S_2}}\right)^{1/2}$	Equilibrium Time	Ca/S	Fe/S	wt%S	$\log C_s$	Melt
108771	1400°C	0.5	2.003×10^{-4}	48 HR	1 (CaO + Illinois Coal Ash)	—	0.48%	-4.02	Yes.
108769	"	"	"	48 HR	1 (CaO + Illinois Coal Ash + 10% B_2O_3)	—	1.60%	-3.49	Yes.
108777	1400°C	0.5	2.003×10^{-4}	47 HR	1 (CaO + Ill. Coal Ash + 5% B_2O_3)	—	0.46%	-4.04	Yes.
108778	"	"	"	"	1 (CaO + Ill. Coal Ash + 5% CaF_2)	—	0.59%	-3.93	Yes.
108779	"	"	"	"	1 (CaO + Ill. Coal Ash + 5% Fe_2O_3)	—	0.66%	-3.88	Yes.
108780	"	"	"	"	1 (CaO + Ill. Coal Ash + 5% P_2O_5)	—	0.27%	-4.27	Yes.

Table X (continue)

Sample #	Temperature (°C)	S.R.	$\left(\frac{P_{O_2}}{P_{S_2}}\right)^{1/2}$	Equilibrium Time	Ca/S	Fe/S	wt%S	$\log C_s$	Melt
108781	1200°C	0.5	1.496×10^{-5}	48 HR	1(CaO+Ill. Coal Ash + 10% B_2O_3)	—	0.59%	-5.05	Yes.
108782	"	"	"	"	2(CaO+Ill. Coal Ash + 10% B_2O_3)	—	2.29% Ave = (2.445)	(-4.44)	(Partially Molten)
108783	"	"	"	"	2(CaO+Ill. Coal Ash + 10% B_2O_3)	—	2.60		

ΤR — LAB SAMPLE
TRACKING REPORT
WORK REQUEST

PROJECT NO. 8518-20 CHARGE NO. 8518-20
ENGINEER Bruce Li
REMARKS: Sent out to Hazen

SAMPLE* NO.	SAMPLE DESCRIPTION	ANALYSIS REQUIRED	SAMPLE PREPARATION	DATE DELIVERED	Fl. (°F) DATE COMPLETED	COMMENTS Fl.(°F)
12-10-1	Ca/S=1	Fusing Temp < Reducing Oxidizing	Bruce Li	12-10-85	[illegible] [illegible]	3g, (2140) (2278)
12-10-2	Ca/S=1, 5% Fe_2O_3	Fusing Temp (Reducing Only)	"	"	2155. ✓	3.053g, (2245)
12-10-3	Ca/S=1, 5% P_2O_5	Fusing Temp. (Reducing Only)	"	"	2141.	3.053g, (2235)
12-10-4	Ca/S=1, 5% B_2O_3	" " "	"	"	[illegible]	3.054g (2020)
12-10-5	Ca/S=1, 5% CaF_2	" " "	"	"		3.4044g. (21[illegible]5)
12-10-6	Ca/S=1, 10% CaF_2	" " "	"	"	[illegible] ✓	3.4241g,
12-10-7	Ca/S=1, 5% CaF_2 5% B_2O_3	" " "	"	"	[illegible]	3.4044g,
12-10-8	Ca/S=1, 5% B_2O_3 5% Fe_2O_3	" " "	"	"	'	3.0 g,
12-10-9	Ca/S=2,	Fusing Temp. (Reducing Only)	"	"		3g.
12-10-10	Ca/S=2, 5% Fe_2O_3	" " "	"	"		3.053g
12-10-11	Ca/S=2, 5% P_2O_5	" " "	"	"		3.053g

* PLEASE PUT IN ORDER OF PRIORITY FOR ANALYSIS

LAB SAMPLE
TRACKING REPORT
WORK REQUEST

PROJECT NO. 8518-20 CHARGE NO. 8518-20
ENGINEER Bruce Li
REMARKS: Sent out to Hazen

SAMPLE* NO.	SAMPLE DESCRIPTION	ANALYSIS REQUIRED	SAMPLE PREPARATION	DATE DELIVERED	DATE COMPLETED	COMMENTS
12-10-12	Ca/S=2, 5% B_2O_3	Fusing Temp. (Reducing Atm)	Bruce Li	12-10-85	2580 ✓	3.054g
12-10-13?	Ca/S=2, 5% CaF_2	" "	"	"	2447. ✓	4.8784g. (2520)

* PLEASE PUT IN ORDER OF PRIORITY FOR ANALYSIS

HAZEN
Hazen Research, Inc.
4601 Indiana St. • Golden, Colo. 80403
Tel: (303) 279-4501 • Telex 45-860

DATE January 8, 1985
HRI PROJECT 009-27
HRI SERIES NO. 31746-A
DATE RECD. 12/16/85
CUST P.O.# None Rec'd.
PROJECT # 8518-20

Energy & Environmental Research Corp.
Mr. Timothy C. Grogan
18 Mason
Irvine, California 92714

REPORT OF ANALYSIS

SAMPLE	SAMPLE	REDUCING ATMOSPHERE				OXIDIZING ATMOSPHERE			
NO.	IDENTIFICATION	IT	ST	HT	FT	IT	ST	HT	FT
31746-1	12-10-1	2120	2165	2175	2197	2130	2169	2175	2200

By:
Gerard H. Cunningham
Coal Laboratory Manager

HAZEN

Hazen Research, Inc.
4601 Indiana St. • Golden, Colo. 80403
Tel: (303) 279-4501 • Telex 45-860

DATE January 8, 1985
HRI PROJECT 009-27
HRI SERIES NO. 31746-B
DATE RECD. 12/16/85
CUST P.O.# None Rec'd.
PROJECT # 8518-10

Energy & Environmental Research Corp.
Mr. Timothy C. Grogan
18 Mason
Irvine, California 92714

REPORT OF ANALYSIS

SAMPLE NO.	SAMPLE IDENTIFICATION	REDUCING ATMOSPHERE			
		IT	ST	HT	FT
31746-2	12-10-2	2076	2140	2150	2165
-3	12-10-3	2050	2080	2090	2140
-4	12-10-4	1885	1935	1950	1975
-5	12-10-5	2135	2170	2180	2193
-6	12-10-6	2114	2160	2170	2186
-7	12-10-7	1885	1951	1960	1982
-8	12-10-8	1850	1900	1930	1958
-9	12-10-9	2682	>2700	-	-
-10	12-10-10	2530	2600	2655	2675
-11	12-10-11	2675	2680	2687	2695
-12	12-10-12	2255	2525	2550	2580
-13	12-10-13	2142	2264	2285	2447

By:
Gerard H. Cunningham
Coal Laboratory Manager

HAZEN

Hazen Research, Inc.
4601 Indiana St. • Golden, Colo. 80403
Tel: (303) 279-4501 • Telex 45-860

DATE January 14, 1986
HRI PROJECT 009-27
HRI SERIES NO. 31746-P
DATE RECD. 12/16/85
CUST P.O.# None Rec'd.
PROJECT # E516-20

Energy & Environmental Research Corp.
Mr. Timothy E. Grogan
18 Mason
Irvine, California 92714

REPORT OF ANALYSIS

SAMPLE NO.	SAMPLE IDENTIFICATION	REDUCING ATMOSPHERE IT	ST	HT	FT	OXIDIZING ATMOSPHERE IT	ST	HT	FT
31746-1	12-10-1	2174	2180	2186	2190	2200	2240	2255	2276

[illegible]
[illegible]

HAZEN

Hazen Research, Inc.
4601 Indiana St. • Golden, Colo. 80403
Tel: (303) 279-4501 • Telex 45-860

DATE January 14, 1986
HRI PROJECT 009-27
HRI SERIES NO. 31746-B
DATE RECD. 12/16/85*
CUST P.O.# None Rec'd.
PROJECT # 8518-20

Energy & Environmental Research Corp.
Mr. Timothy L. Grogan
18 Mason
Irvine, California 92714

REPORT OF ANALYSIS

SAMPLE NO.	SAMPLE IDENTIFICATION	REDUCING ATMOSPHERE			
		IT	ST	HT	FT
31746-2	12-10-2	2115	2210	2225	2245
-3	12-10-3	2160	2180	2200	2235
-4	12-10-4	1973	1995	2005	2020
-5	12-10-5	2150	2178	2184	2195
-13	12-10-13	2197	2393	2430	2520

[illegible]
Coal Laboratory [illegible]

[illegible]

1/22/86 Table X.

		Ca/S=1 (Fluid Temp. at Reducing Conditions = 2194°F)				Ca/S=2 (Fluid Temp. at Reducing Conditions >2700°F)			
Additives Fluid Temp. (°F) % additive		100% Purity Fe_2O_3	99.7% Purity P_2O_5	98.9% Purity B_2O_3	99.% Purity CaF_2	100% Purity Fe_2O_3	99.7% Purity P_2O_5	98.9% Purity B_2O_3	99.% Purity CaF_2
5% Additives	1st Run	2165.	2140.	1975.	2193.	2675.	2695.	2580.	2580
	2nd Run	2245.	2235.	2020.	2195.	—	—	—	2520
Average	5%	2205.	2188.	1998.	2194	2675.	2695.	2580.	2550.
	10%	2183.	2245.	1933.	2186.	2557.	2639.	2255.	2507.
10% Additives	1st Run	2203.	2294.	1935.	—	2580.	2668.	2305.	2484.
	2nd Run	2162.	2196.	1930.	2186.	2533.	2609.	2205.	2530.

Note: All the analysis results are reported from Hazen Research, Inc.